이학박사학위논문

Biogeochemical characteristics and fluxes of wet depositional organic matter in urban versus rural regions

도심과 교외 지역에서 강수 중 유기물의 생지화학적 특성과 플럭스에 관한 연구

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Biogeochemical characteristics and fluxes of wet depositional organic matter in urban versus rural regions

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A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the School of Earth and Environmental Sciences, Seoul National University, in

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Abstract

Biogeochemical characteristics and fluxes of wet depositional organic matter in urban versus rural regions

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Organic matter is a significant and ubiquitous chemical constituent in the atmosphere, which plays crucial roles in multiple aspects, ranging from climate change to human health. In addition, it has increasingly been recognized to constitute an important part of global biogeochemical cycles and nutrient budgets, the knowledge on which is, however, rather limited. In order to improve our understanding of the significant role of atmospheric organic matter in biogeochemical cycling, the sources, fluxes, and biogeochemical characteristics of dissolved organic matter in precipitation were investigated at two representative sites (Seoul and Uljin) of Korea based on a long-term survey (2009–2013).

The concentrations of dissolved organic carbon (DOC) at Seoul varied from 15 μM to 780 μM, with a volume-weighted average of 94 μM. Using the commonly acknowledged tracers, the combustion of fossil-fuels was recognized to be the dominant source. With the aid of air mass backward trajectory analyses,

I concluded that the primary fraction of DOC in the precipitation samples originated locally in Korea, albeit the frequent long-range transport from eastern and northeastern China might contribute substantially. In light of the relatively invariant organic carbon to sulfur mass ratios in precipitation over Seoul and other urban regions around the world, the global magnitude of wet depositional DOC originating from fossil-fuels was further calculated to be 36 ± 10 Tg C yr^{-1}.

In precipitation collected at Uljin, air mass back trajectory analysis revealed that a significant fraction of the inorganic nitrogen (NO_3^- and NH_4^+) originated from mainland Asia, whereas the DON was primarily derived from Korea. Using varimax-rotated factor analysis in combination with major ions as tracers, agricultural activities in Korea were identified as the primary sources of DON. In addition, a positive correlation was found at Uljin between the size of organic fraction in total reactive nitrogen and nitrogen to carbon atomic ratio in organic matter. This correlation has also been observed at other locations worldwide, implying the utilization potential of atmospheric organic nitrogen might increase with its proportion in total nitrogen. Combining wet deposition measurements in this study with literature values for dry deposition observed at a remote island in the East/Japan Sea (EJS), the total atmospheric depositional flux of reactive nitrogen was estimated to be 115 mmol N m^{-2} yr^{-1} over the southern EJS. These results shed new light on the potentially significant contribution to primary productivity of the northwestern Pacific Ocean by atmospheric deposition of nitrogen, especially the organic fraction.

The average concentrations of DOC, DON, and total hydrolyzable amino acids at Seoul (an inland urban area) were found to be lower than those at Uljin (a

coastal rural area). The different bulk compositions of dissolved organic matter (DOM) at these two sites (reflected by qualitative indicators) were mainly attributed to differences in contributing sources. The D-enantiomers of four individual amino acids (aspartic acid, glutamic acid, serine, and alanine) were ubiquitously present in precipitation samples. The much higher D/L ratios observed at Seoul than at Uljin might result from more advanced diagenetic stages as well as higher contributions from bacteria inhabiting terrestrial environments. The C- and N-normalized yields of D-alanine in DOM in precipitation samples were found to be comparable to literature values reported for aquatic systems, where a significant portion of DOM was suggested to be of bacterial origin. These results suggest that bacteria and their remnants might constitute an important fraction of OM in the atmosphere, contributing significantly to the quality of atmospheric OM and its post-depositional bioavailability in the surface ecosystems.

This study contributes to our understanding of OM in the atmosphere from the biogeochemical perspective. It further underscores the necessity of extensive future researches to obtain more comprehensive knowledge regarding the biogeochemical role of atmospheric organic matter, such as chemical speciation and bioavailability.

Keywords: Organic matter, Biogeochemical cycles, Atmosphere, Wet deposition, Organic carbon, Organic nitrogen

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1. Introduction

1.1. Organic matter in the atmosphere: Cycling and composition

The early studies on organic matter (OM) in the atmosphere date back to the 1950s (e.g., Haagen-Smit, 1952; Mader et al., 1952). Thereafter, the work by Went (1960) first suggested the potential importance of the organically derived blue hazes to the atmospheric radiative balance and catalyzed the early interests in atmospheric OM. However, extensive attention on atmospheric OM has only been attracted from the scientific community since Duce et al. (1983) published a review on global tropospheric OM and emphasized its importance. It is now well known that OM is a significant and ubiquitous chemical constituent in the atmosphere, playing crucial roles in a variety of fields (Fig. 1.1), such as the Earth's climate (modifying the radiative balance both directly through scattering and absorption of solar radiation, and indirectly through formation of cloud condensation nuclei) (IPCC, 2007), human health (through the spread of reproductive materials and micro-organisms, impacts on respiratory and cardiovascular functions, and allergic diseases) (Fuzzi, 2006; Delfino et al., 2010), air quality (Kanakidou et al., 2005), visibility (Seinfeld and Pandis, 1998), and atmospheric physico-chemical processes (Monks et al., 2009).

As illustrated in Fig 1.2, OM in the atmosphere is derived directly or indirectly from both living and dead organisms during a variety of natural and anthropogenic processes. The direct pathway encompasses any kinds of biogenic emissions by plants and animals in terrestrial and marine systems; whereas the indirect mechanism mainly refers to incomplete combustion processes involved

with relic (fossil-fuel) and modern plant as well as animal tissues. A large fraction of atmospheric OM resides in the aerosol phase (solids and liquids, the remaining are gaseous), which can be either emitted directly from any potential sources (primary organic aerosol) or formed as secondary organic aerosol from gaseous volatile organic compounds via gas-to-particle conversions. The anthropogenic processes (mainly biomass and fossil-fuel burning) have been found to be the dominant sources of primary organic aerosols (Chung and Seinfeld, 2002), as well as significant contributors to secondary organic aerosols, of which the anthropogenically derived fraction was recently suggested to be underestimated (Henze et al., 2008). In particular, previous studies based on carbon isotopic analyses (^{13}C and ^{14}C) suggest that approximately 20–30% of dissolved organic carbon in rainwater is of fossil-fuel origin (Avery et al., 2006; Raymond, 2005). After being emitted, OM often undergoes various transformation processes (atmospheric aging) in the atmosphere (particularly in clouds), during which its chemical and physical properties (e.g., structure and composition) can be dramatically changed. Aside from a considerable fraction of gaseous OM being oxidized to CO_2 (mainly via CO), the remaining portion and particulate OM (organic aerosols) are ultimately scavenged from the atmosphere and returned to the Earth's surface by either wet or dry deposition (Goldstein and Galbally, 2007; Hallquist et al., 2009). The wet deposition, which removes OM residing in clouds (rainout) as well as suspending in the atmosphere (washout), is generally thought to be the main sink of atmospheric OM. Although less important on a global scale, the dry deposition (convective transport, diffusion, and adhesion) of atmospheric

OM may play an important role in local or regional air quality and biogeochemical cycles.

Due to the numerous organic compounds potentially present in the atmosphere, characterizing atmospheric OM is extremely challenging (Goldstein and Galbally, 2007). Our understanding of the chemical speciation of atmospheric OM is also limited by the availability of analytical techniques (Hallquist et al., 2009). In the case of organic aerosols, hundreds of organic compounds have been detected by previous studies. However, even in the most comprehensive investigations, only 10 to 40% of the OM has been unambiguously identified on a molecular level (Pöschl, 2005). The dominant organic compound classes present in aerosols include levoglucosan, fatty acids and other alkanoic acids, aliphatic dicarboxylic acids, aromatic (poly-) carboxylic acids, proteins and other amino compounds, secondary organic oligomers/polymers and humic-like substances (Fig. 1.3). In rainwater, organic acids could contribute to 14–36% of dissolved organic carbon (DOC) pool, with other known compound classes (e.g., aldehydes, amino acids) contributing less than 10% (Avery et al., 2006). Approximately 50% of DOC remains uncharacterized at both the compound class and individual compound level (Willey et al., 2000). The lack of knowledge on compositions of atmospheric OM greatly hinders our understanding of its impact on the Earth's environment.

1.2. Potentially significant roles of atmospheric organic matter in biogeochemical cycles

The OM pool consists of multiple bioreactive elements, such as C, N, and P, thus constitutes an important part of global biogeochemical cycles and nutrient budgets. In addition, the atmospheric deposition allows OM to be transported to locations remote from their source regions over relatively short time scales. Therefore, although most studies on atmospheric OM are driven by its significant roles in climate and public health, there is increasing interest in its potential impacts on marine and terrestrial biogeochemical cycles (Willey et al., 2000; Duce et al., 2008; Cornell, 2011; Kanakidou et al., 2012).

It has been found by Willey et al. (2000) that DOC is a major component of both marine and continental rain present in concentrations greater than nitric and sulfuric acids combined. An estimation of global rainwater flux of DOC of 430 ± 150 Tg C yr^{-1} was reached based on a comprehensive review of worldwide published rainwater DOC concentrations during the late 1990s (Willey et al., 2000). The DOC input via wet deposition to surface seawater was estimated to be 90 Tg C yr^{-1}, which is equivalent to the magnitude of river input of DOC to the open ocean and half the magnitude of carbon buried in marine sediments per year on a global scale (Willey et al., 2000). Bauer and Bianchi (2011) estimated that atmospheric organic carbon derived from fossil-fuel combustion may potentially account for as much as 10–20% of total organic carbon exported globally by rivers to the coastal ocean on an annual basis. Moreover, the annual mean depositional fluxes of aerosol-derived organic carbon scaled to the Hudson and York River (USA) watersheds were found to be similar in magnitude to that

through river export for these two systems (Wozniak, 2009). In addition, there are a growing number of studies suggesting atmospheric organic nitrogen plays an important role in the global nitrogen cycle, contributing to ca. 30% of atmospheric reactive nitrogen deposition (Jickells, 2006; Cape et al., 2011; Cornell, 2011). Model results show that each year 16–20 Tg organic nitrogen is transported to global oceans through atmospheric deposition (Duce et al., 2008; Kanakidou et al., 2012).

After being deposited to the surface ecosystems, atmospheric OM is subject to degradation or preservation processes, depending on the chemical nature of OM and the environmental conditions, as well as organism community structure of the receiving systems. Avery Jr. et al. (2003) found that the bioavailable fraction of rainwater DOC is around 60% based on laboratory experiments, which is significantly higher (approximately 6 times) than that of riverine DOC. In addition, incubation experiments estimate the bioavailability of atmospheric organic nitrogen to be 20–80% (Peierls and Paerl, 1997; Seitzinger and Sanders, 1999; Wedyan et al., 2007).

It can be seen that atmospheric OM is quantitatively significant and largely bioavailable, thus may play a significant role in the biogeochemical cycling and nutrient budgets. In addition, it has been suggested that human activities have significantly modified the composition, magnitude, and transport of atmospheric OM, and this trend would be continued in the future (Kanakidou et al., 2012), implying the changing biogeochemical role of atmospheric OM should be carefully monitored. However, although some efforts have been made by previous workers to characterize its biogeochemical role, quantitative and qualitative

studies on atmospheric OM deposition are still in an early stage of development, with large uncertainties in knowledge regarding source, composition, bioavailability, and the environmental impacts (Bauer and Bianchi, 2011, Kanakidou et al., 2012).

1.3. Aim of this study

The overall goal of this study is to contribute to advancing our knowledge regarding the biogeochemical role of atmospheric OM based on field observations conducted in Korea. Since precipitation samples could provide a comprehensive view of atmospheric OM (through in-cloud and below-cloud scavenging) within the atmospheric boundary layer, this study focuses on OM in wet deposition. Carbon and nitrogen are the main subjects of this dissertation, as they are the primary bioreactive elements that comprise OM pool. The specific objectives of this study are:

(1) to investigate the sources and fluxes of DOC in precipitation collected at an inland urban area of Korea (Seoul) and further to estimate the global magnitude of wet depositional DOC originating from fossil-fuels;

(2) to examine the distributions and characteristics of DOM and to evaluate the contributions from bacteria and its remnant to DOM in precipitation collected at Seoul and Uljin (a coastal rural area) of Korea; and

(3) to determine the geographical and emission sources as well as fluxes of DON in precipitation collected at Uljin and further to estimate the contribution from atmospheric DON deposition to new primary productivity of the adjacent East/Japan Sea.

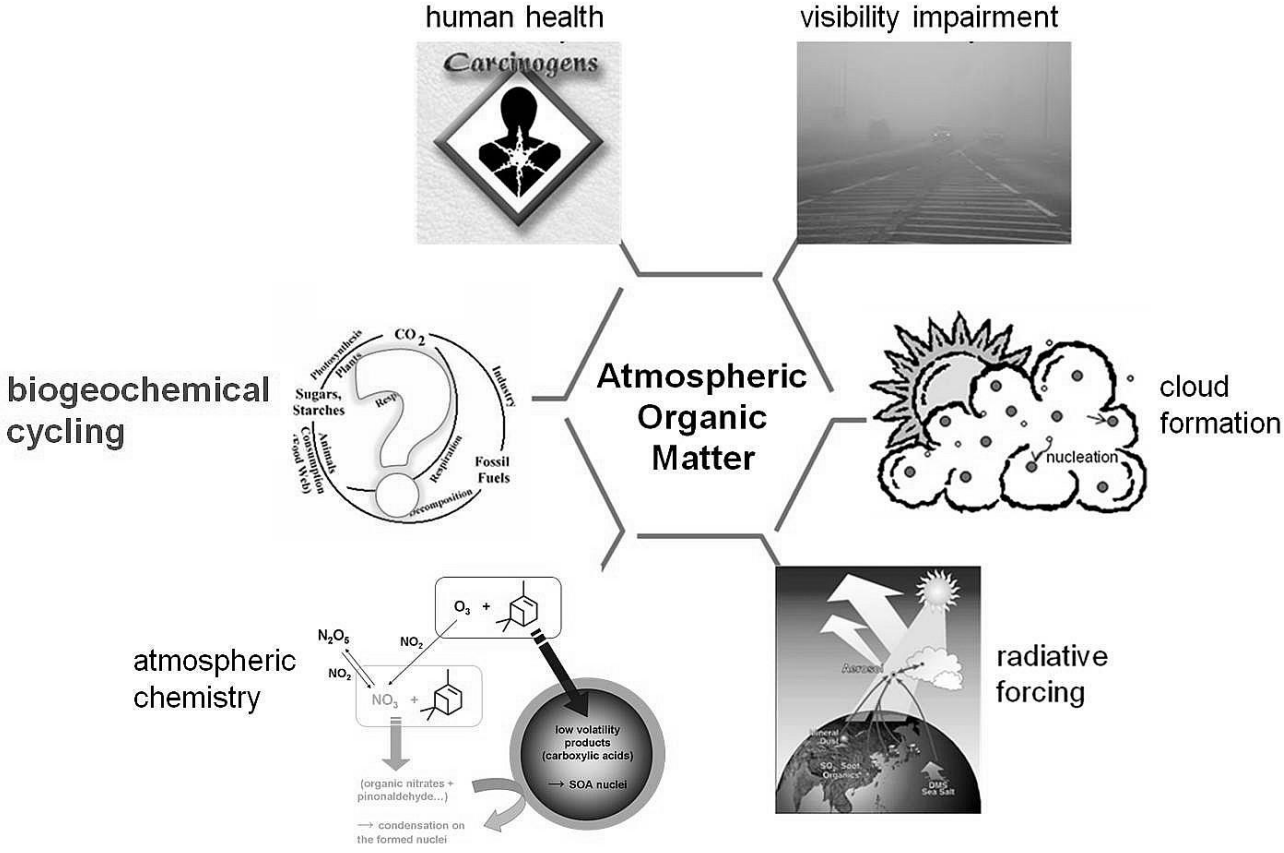


Figure 1.1. Significant roles of atmospheric organic matter in the Earth's environment.

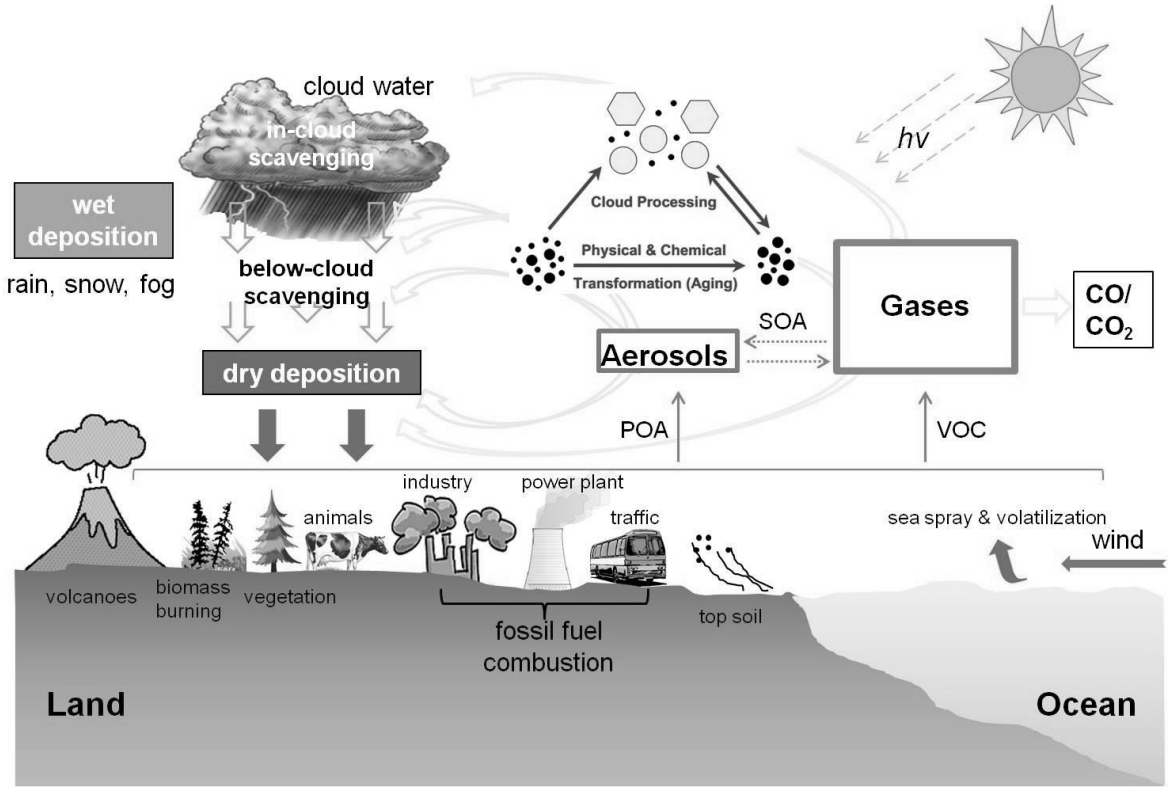


Figure 1.2. Schematic illustration of organic matter cycling in the atmosphere showing the various emission sources, transformation pathways, and major sinks. Abbreviations: POA, primary organic aerosol; SOA, secondary organic aerosol; VOC, volatile organic compound.

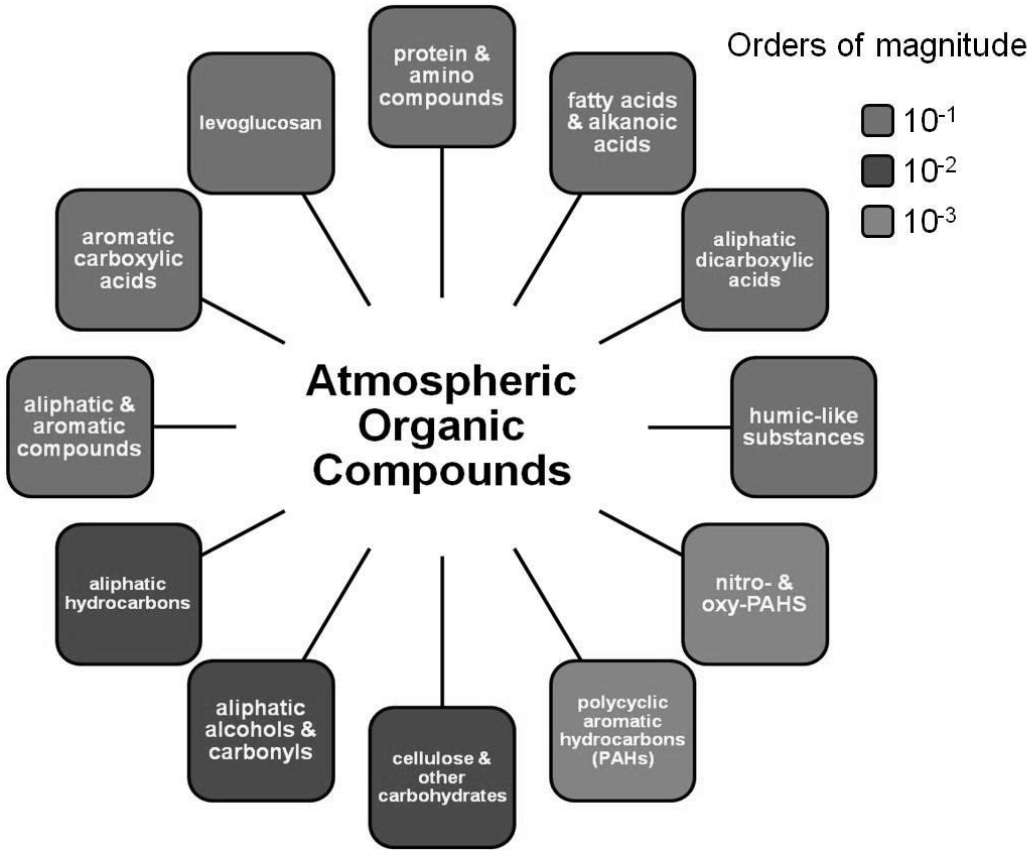


Figure 1.3. Prominent organic compound classes identified in aerosols (based on Pöschl, (2005)).

2. Materials and methods

2.1. Analysis of major ions

Major ions including inorganic nitrogen species were determined by high performance liquid chromatography using a Waters 2695 HPLC system equipped with a Waters 432 conductivity detector. Cation analysis (i.e., Na^+, K^+, Ca^{2+}, Mg^{2+}, and NH_4^+) was carried out using a mobile phase consisting of 3.0 mmol L^{-1} HNO_3 and 0.1 mmol L^{-1} EDTA, and a Waters IC-Pak C M/D column (150 × 3.9 mm, 5 μm) (Fig. 2.1). Anions (i.e., Cl^-, NO_3^-, NO_2^-, and SO_4^{2-}) were analyzed using a borate/gluconate eluent containing 12% acetonitrile and a Waters IC-Pak A HR column (75 × 4.6 mm, 6 μm) (Fig. 2.2). The column was maintained at 30 ℃ and the detector at 35 ℃. The flow rate was regulated at 2.0 mL/min for analysis of anions and 1.0 mL/min for cation analysis, respectively. The limits of detection calculated as three times the standard deviation of blanks are 0.2 μmol L^{-1} for Na^+, 0.5 μmol L^{-1} for K^+, 0.4 μmol L^{-1} for Ca^{2+}, 0.4 μmol L^{-1} for Mg^{2+}, 0.5 μmol L^{-1} for NH_4^+, 0.5 μmol L^{-1} for Cl^-, 0.3 μmol L^{-1} for NO_3^-, 0.3 μmol L^{-1} for NO_2^-, 0.8 μmol L^{-1} for SO_4^{2-}, respectively.

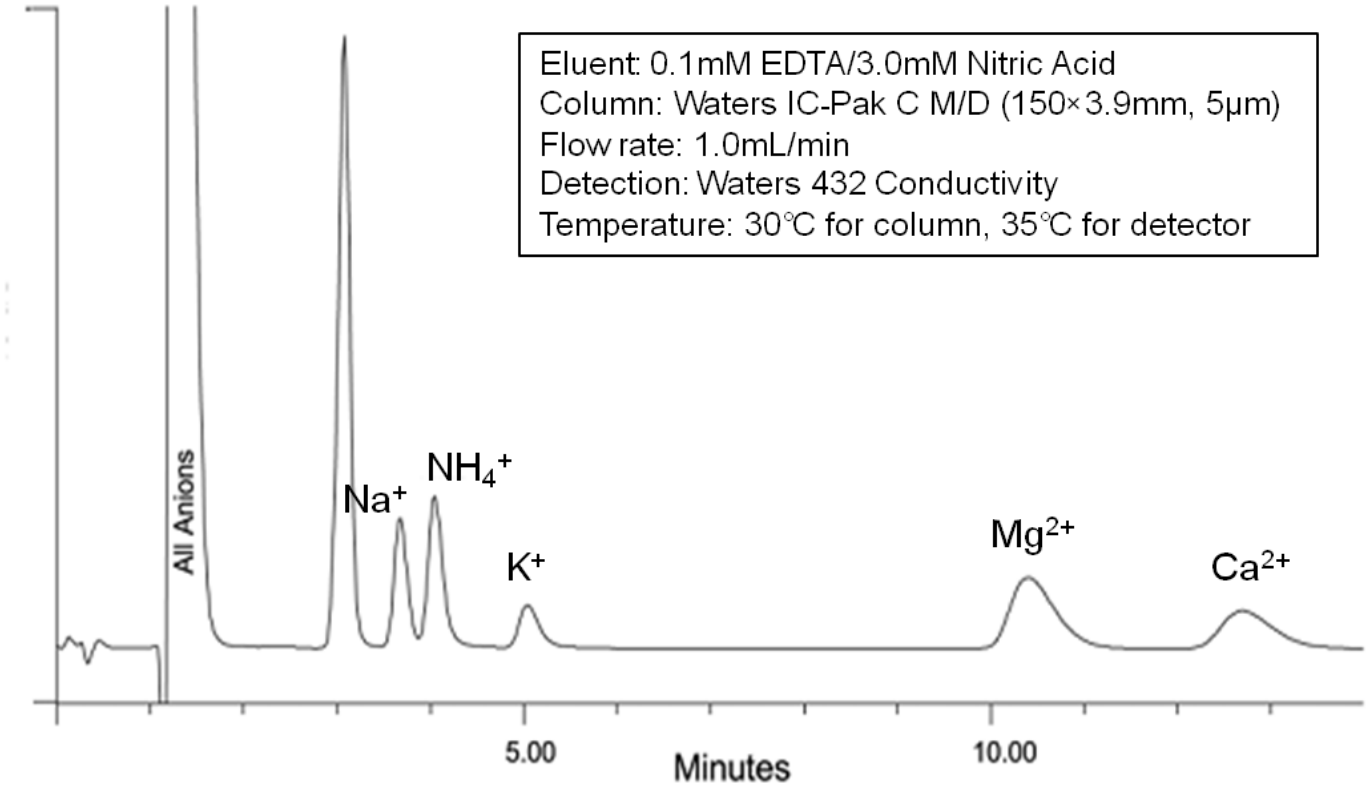


Figure 2.1. Chromatogram of cation standards and the chromatographic conditions used in HPLC system.

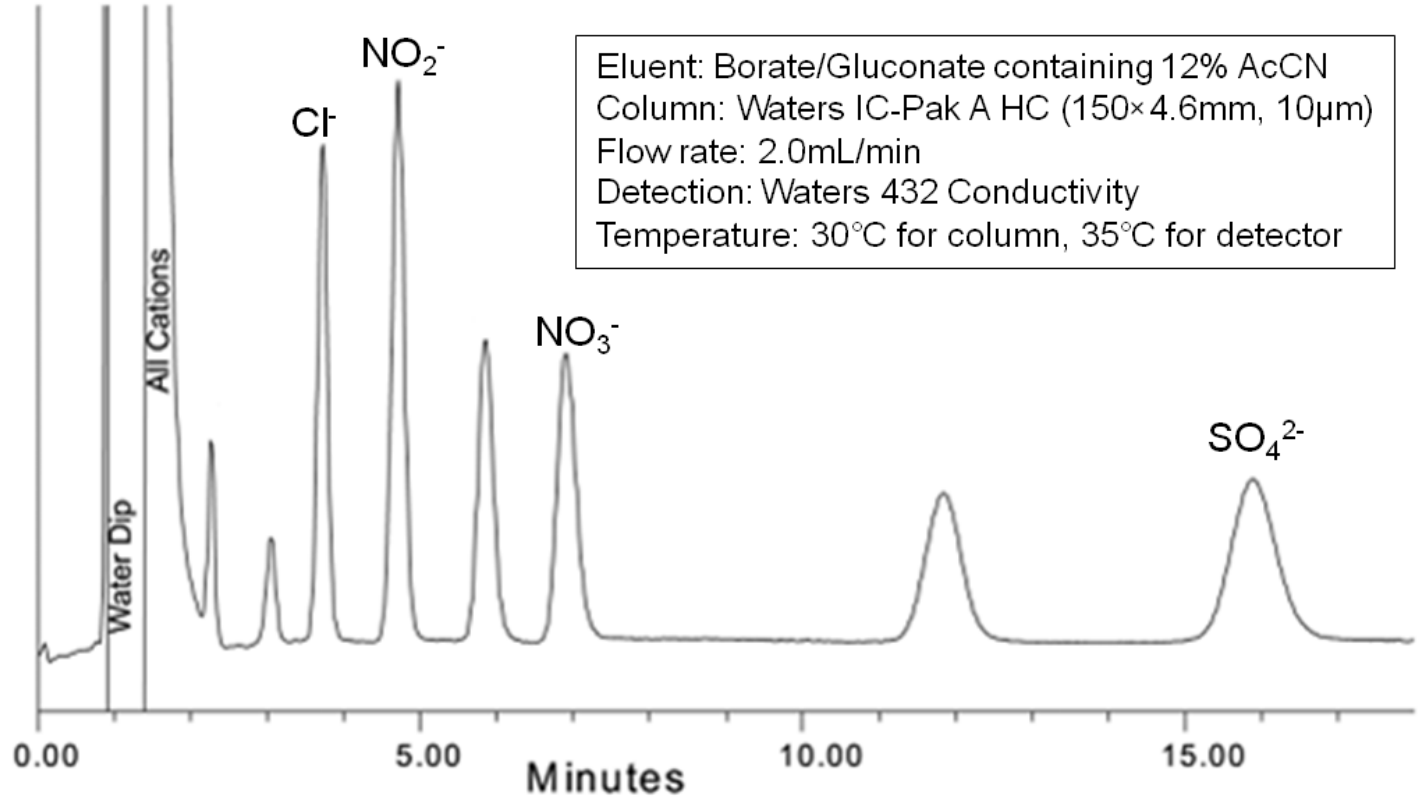


Figure 2.2. Chromatogram of anion standards and the chromatographic conditions used in HPLC system.

2.2. Analysis of DOC and DON

Total dissolved nitrogen (TDN) and DOC concentrations were measured synchronously by high temperature catalytic oxidation (HTCO) using a Shimadzu TOC/TN analyzer (Model TOC-$V_{CPH/CPN}$) equipped with an ASI-V auto-sampler (Fig. 2.3). The standards were prepared from reagent grade potassium hydrogen phthalate in ultra-pure water (resistivity: 18 MΩ cm). The acidified samples were sparged with carbon dioxide free carrier gas (UHP oxygen) at a flow rate of 150 ml/min for 2 min to remove inorganic carbon. Then the samples were injected into a combustion column packed with Pt coated alumina beads heated to 720 ℃. The carbon dioxide and nitrogen monoxide evolving from combustion were detected by a non-dispersive infrared detector and a chemiluminescence detector, respectively. DON was quantified as the difference between TDN and inorganic nitrogen, which is the sum of NO_3^- and NH_4^+ (NO_2^- was not detected in precipitation samples and is therefore not included). This approach could yield considerable uncertainties for DON, especially when inorganic nitrogen dominates the nitrogen pool, as being revealed by previous studies (Sharp et al., 2002; Cornell et al., 2003). The average relative standard deviations associated with replicate measurements of standards were 4%, 2%, and 3% for TDN, NO_3^-, and NH_4^+, respectively. Based on error propagation using uncertainties of each analyte, the analytical errors of DON were estimated to be less than 20% when DON/TDN is greater than 20%, 20–80% when DON/TDN varies from 5% to 20%, and greater than 100% when DON/TDN is less than 5%. The detection limits of the analytic methods are 2.5 μmol L^{-1} for TDN, and 5.0 μmol L^{-1} for DOC, respectively. The detection limit for DON was estimated to be 1 μmol L^{-1} (Cornell

et al., 1998; Zhang et al., 2001). The quality of the data was assured by inserting certified reference materials (from University of Miami) in each run of samples, for which the measured results agreed to within 5% of authentic values. The blank during collection and filtration was determined as the difference before and after the sampling and processing procedures using ultra-pure water and subtracted from sample concentrations.

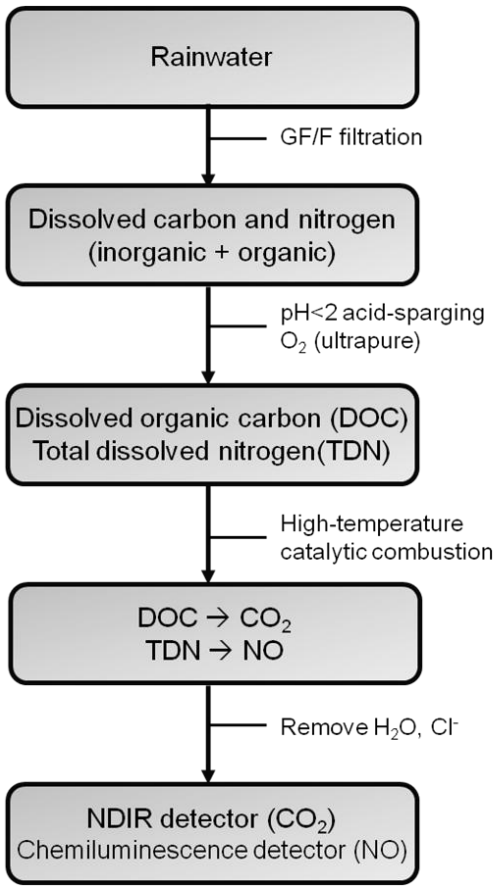


Figure 2.3. Schematic diagram showing the procedures for determination of DOC and TDN using HTCO method.

2.3. Analysis of enantiomeric total hydrolyzable amino acids

Amino acids were analyzed by using reverse-phase high performance liquid chromatography (HPLC) according to Fitznar et al. (1999) and Dittmar et al. (2009) (Fig. 2.4). Prior to analysis, the samples were hydrolyzed first to liberate amino acids in the combined form. Briefly, in a class-100 clean bench, 1 mL of sample and 1 mL of 12 M hydrochloric acid (ACS grade, Sigma-Aldrich) were transferred into a 2-mL glass ampoule (pre-combusted at 500 ℃), followed by addition of 10 μL of 11mM ascorbic acid prepared using Milli-Q water (18.2 MΩ cm). After being flushed with ultra pure nitrogen gas for about 1 minute, the glass ampoule was fire sealed. The sealed ampoule was then placed in a convection oven, where the sample was hydrolyzed at 110±2 ℃ for 24 hours. During this step, asparagine and glutamine were deaminated and transformed to aspartic acid and glutamic acid, respectively. Thereafter, 1 mL aliquot of the hydrolysate in the ampoule was transferred to a standard autosampler glass vial (Waters, pre-combusted at 500 ℃), and lyophilized using a freeze-drier. The residue was then re-dissolved in 0.5 mL pH adjusted Milli-Q water (the final pH of solution was 8~9), and stored frozen at -20 ℃ until analysis.

Glycine (Gly), amino butyric acid (GABA), and the enantiomers of the individual amino acids aspartic acid (Asp), glutamic acid (Glu), serine (Ser), threonine (Thr), arginine (Arg), alanine (Ala), , tyrosine (Tyr), valine (Val), phenylalanine (Phe), isoleucine (Iso), and leucine (Leu) were analyzed by using HPLC after pre-column derivatization with o-phthaldialdehyde (OPA) and N-isobutyrylcysteine (IBC) (Fitznar et al., 1999; Dittmar et al., 2009) (Fig. 2.5). The HPLC system employed was Waters 2695 equipped with an Alltech Alltima HP

C18 column (5μm, 4.6x150mm) and a Waters 2475 fluorescence detector. The derivatization was performed manually by mixing 500 μL of hydrolyzed sample with 20 μL of OPA (37 mM in pH 9.5 borate buffer) and 20 μL of IBC (26 mM in a mixture of water and methanol at a ratio of 6:4) 5 minutes before injection into the chromatographic system. A linear solvent gradient was used after Dittmar et al. (2009), which consists of two solvents (25 mM sodium acetate buffer with pH adjusted to 6 and 100% HPLC grade acetonitrile). The flow rate was 1.1 mL min^{-1} and column temperature was maintained at 30 ℃. After being separated via the reversed phase C18 column, the amino acid derivatives were monitored by fluorescence detection at an excitation wavelength of 330 nm and an emission wavelength of 445 nm. For calibration and quantification, a standard mixture of 13 individual amino acids (Sigma-Aldrich) was used. Procedural blanks determined using Milli-Q water in place of samples were subtracted from measured sample concentrations. Chemical racemization occurred during acidic hydrolysis was corrected using the average rates determined on free and protein amino acids by Kaiser and Benner (2005) under similar conditions. The analytical method used in this study did not distinguish between free and combined forms of amino acids, so the results represent total hydrolyzable amino acids (THAA).

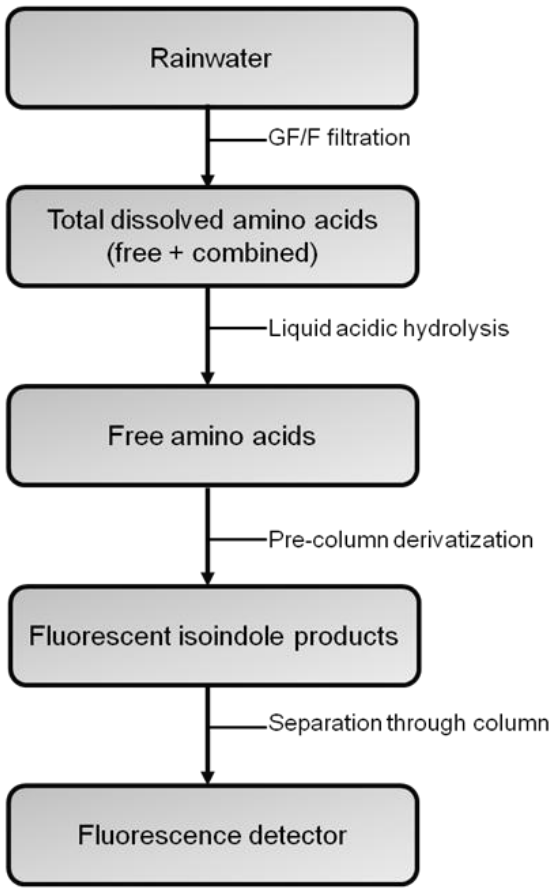


Figure 2.4. Schematic diagram showing the procedures for determination of enantiomeric total hydrolyzable amino acids using HPLC.

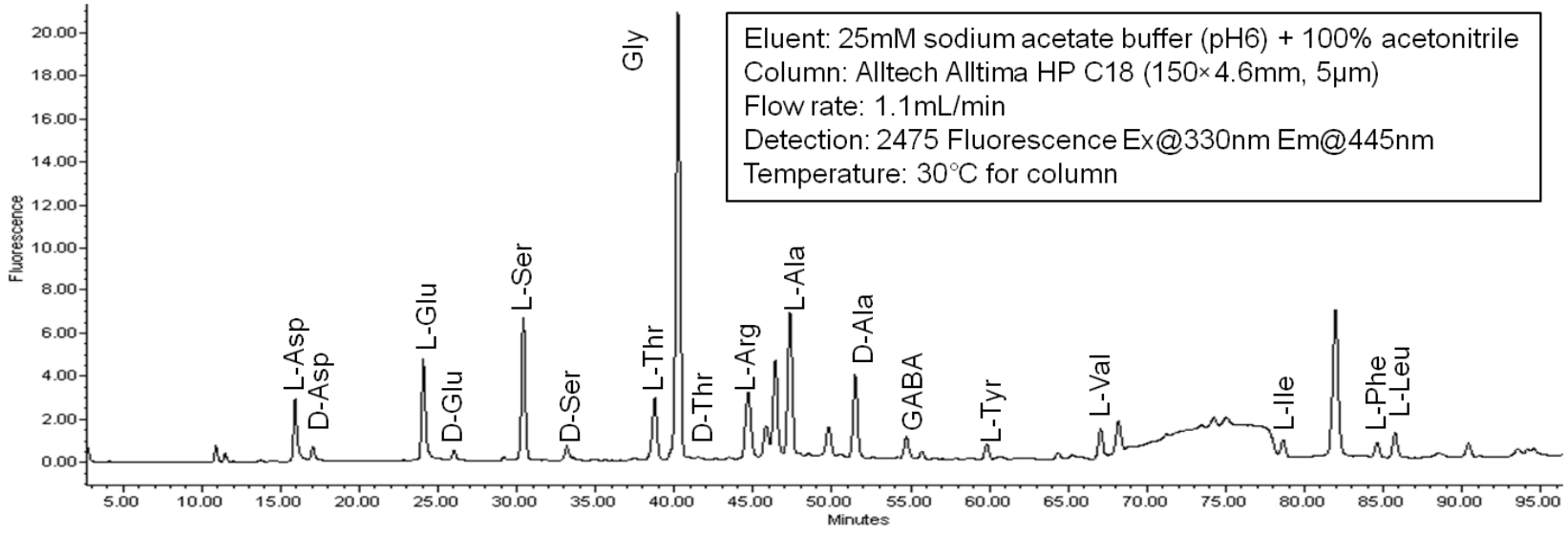


Figure 2.5. Chromatogram of enantiomeric amino acids in a rainwater sample and the chromatographic conditions used in HPLC system.

2.4. Analysis of trace elements

The trace elements (aluminum and vanadium) were analyzed using an inductively coupled plasma mass spectrometer (ICP-MS, Model: X-II, Thermo Inc., UK) equipped with a MicroMist nebulizer (Glass expansion, USA). Rhodium (SCP, Canada) was used as the internal standard. Certified reference materials (CASS-4 and NASS-5, National Research Council of Canada) were employed during the sample analysis to confirm the data quality, the results of which agreed to within 10% of the authentic values.

2.5. Air mass backward trajectory analysis

The air mass transport pathways for all the precipitation events were determined based on air mass back-trajectories produced using version 4 of the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (http://www.arl.noaa.gov/ready/hysplit4.html) developed at the Air Resources Laboratory of NOAA (Draxler and Hess, 1998) and the GDAS dataset. Backward trajectories were calculated for 72 h hind-cast starting at 500 m above ground level, corresponding to the well-mixed boundary layer, which is likely to contribute more heavily to in-cloud processes and wet deposition (Walker et al., 2000). Discrepancies were found in output back trajectories when different altitudes were used (e.g., 1000 m and 1500 m). In addition, due to the limitation of meteorological data resolution, an individual trajectory might be subject to an uncertainty of 20–30% of the travel distance (Stunder, 1996; Draxler and Hess, 1998). However, these uncertainties have no significant impact on the application of the trajectories in this study.

3. Dissolved organic carbon in the precipitation of Seoul, Korea: Implications for global wet depositional flux of fossil-fuel derived organic carbon

3.1. Introduction

The contemporary issue of global warming has been mainly attributed to the elevated carbon dioxide level in the atmosphere arising from various human activities since the industrial revolution. A reliable assessment of human impact on future climate change therefore rests with a full understanding of the global biogeochemical carbon cycle. However, the global carbon budget pertaining to anthropogenic perturbation based solely on inorganic carbon is unable to account for the fate of ca. 20% of global carbon dioxide, which is referred to as "the missing carbon sink". Previous studies (Coelho et al., 2008; Jurado et al., 2008; Kieber et al., 2002; Orlović-Leko et al., 2009; Pan et al., 2010; Willey et al., 2000) highlight the significance of incorporating atmospheric organic carbon (OC) into the models of the global carbon cycle. OC in the atmosphere can be ultimately transformed into carbon dioxide either by in-situ oxidation (Goldstein and Galbally, 2007; Willey et al., 2000) or by biochemical degradation at the Earth's surface after being scavenged from the atmosphere. Therefore, it is of great importance to integrate an unequivocal representation of this potentially significant carbon reservoir, especially the anthropogenic fraction, into the global models. Since precipitation is considered to be the dominant scavenging mechanism in the atmosphere, wet depositional flux is generally employed to elucidate the quantitative information for most airborne species. An estimation of

global rainwater flux of dissolved organic carbon (DOC) of 430±150 Tg C yr^{-1} has been reached by Willey et al. (2000) based on a comprehensive review of worldwide published rainwater DOC concentrations during the late 1990s. Nevertheless, large discrepancy (144 Tg C yr^{-1} for input to the oceans only) between this global approximation and that derived from another approach (Jurado et al., 2008, wet depositional flux using models) implies that the rainwater measurement based calculation might be subject to considerable uncertainties, which are deemed to be at least partially attributable to the paucity of quantitative knowledge (Jurado et al., 2008; Kieber et al., 2002), as well as the remarkable temporal variations in organic carbon levels in rainwater over the last decade (Willey et al., 2006 and 2011; Xu et al., 2009). Consequently, it is imperative to conduct more extensive surveys on rainwater DOC, especially in Asia, where little information is available.

Seoul is the sixth largest city around the globe in terms of population density and is characterized by intensive industrialization and urbanization. Moreover, Seoul is subject to substantial influences from long-range transport of air pollutants (Kim et al., 2009), since Northeast Asia is one of the largest fossil-fuel combustion regions, with China being recognized as a major source for anthropogenic carbonaceous aerosols (around a quarter of the global budget) (Cooke et al., 1999). Therefore, Seoul is presumably an ideal site to investigate atmospheric OC which stems from or is controlled by human activities. This study presents the abundance level of DOC in precipitations at a location in south-central Seoul over a one-year period, as a contribution to the integrity of the global wet depositional DOC dataset. Furthermore, on the basis of the

identification of DOC sources at this site, I have attempted to undertake a quantitative evaluation of the global magnitude of fossil-fuel derived DOC in rainwater.

3.2. Study site and sample collection

Seoul, as the capital of Korea, is a metropolitan city with over 10 million residents inhabiting an area of 605.36 km^2. It is located in the midwestern part of the Korean Peninsula, approximately 30 km to the east of the Yellow Sea. The climate of Seoul is rather complex with both continental and oceanic features. Our sampling duration is considered to be a wet year with a total precipitation depth of 1816 mm, in comparison with a thirty-year average of 1451 mm (1981–2010, Korea Meteorological Administration). The prevailing wind systems for Seoul are westerlies (southwesterly in the summer and northwesterly in the winter). The primary land-use types of Seoul in descending order of areal percentage are residential (35%), forest (26%), and industrial (12%). Agricultural activities are generally found in the suburban area of western and eastern parts of Seoul. In addition, the western coastal city of Inchon and the surrounding Kyunggi province (along with Seoul are known as the Seoul Metropolitan Region) which are highly industrialized and urbanized may also exert significant impacts on the atmospheric environment of Seoul.

The sampling campaign was carried out on a four-storey building rooftop at the Gwanak campus of Seoul National University in a mixed commercial and residential area of Seoul (37.5 °N, 127 °E) from October 2009 to September 2010. There were no potential pollution sources (e.g. exhaust hoods) in sight around the

sampling spot or any significant emission sources (e.g. smokestack) in the nearby regions. Precipitation samples (rain and snow) were collected on an event basis using a borosilicate glass vessel (pre-combusted at 500 ℃) and a polypropylene vessel (pre-washed with dilute acids) for DOC and other chemical constituents, respectively. The apparatus was manually deployed on a supporting rack 1.2 m above the rooftop at the onset of the precipitation events, and retrieved immediately after cessation. In the case of the events which began or ended at night, samplers were placed in the late evening or recovered in the early morning of the next day (usually within 5 h). Therefore, the bulk samples I collected were also affected by dry deposition. However, its contribution is expected to be minimal, considering the rather limited exposure time to dry conditions and the fact that wet scavenging on the whole is the dominant removal process for most airborne species including carbonaceous aerosols (~80%) (Kanakidou et al., 2005). After collection, the samples were transported to a laminar flow clean room inside the building for processing and preservation. The snow samples were allowed to thaw at room temperature before further treatment. Subsamples for DOC and major ions were filtered using an acid-washed plastic syringe joined to a syringe filter (Whatman GF/F, pore size 0.7 μM). The filtration set was thoroughly rinsed with ultra-pure water before use and pre-conditioned with an aliquot of sample to minimize the risk of contamination. DOC samples were placed in 20 mL pre-muffled glass ampoules and preserved with 6M pure HCl, followed by fire sealing using a hand-held butane burner. Aliquots for the measurement of ions were collected in polypropylene conical tubes and kept frozen at -20 ℃ until analysis. Following the rigorous ultra-clean protocols, in a class-100 clean bench, the

subsamples for trace elements (unfiltered) were transferred to pre-cleaned HDPE bottles and then acidified with 6M ultra-pure HNO_3 (Yan et al., 2012).

3.3. Results and Discussion

3.3.1. DOC levels in precipitation and the controlling factors

The DOC concentration levels in the precipitation samples ranged from 15 μM to 780 μM, with an annual volume-weighted average (VWA) of 94 μM. No significant differences in DOC concentrations were found between rainwater (VWA = 94 μM, N = 49) and snow (VWA = 92 μM, N = 8) samples. The monthly VWA DOC concentrations showed relatively small variations throughout the year, among which slightly higher values were found in cold seasons than those in warm seasons (Fig. 3.1a). The maximum was observed in January, which is associated with the lowest monthly precipitation of the year. The VWA for the growing season (April to September) and non-growing season (October to March) were calculated to be 87 μM and 127 μM, respectively. Several extreme events with concentrations as low as 15 μM have been observed. Because the sampling site is subject to frequent marine influences, especially in summer, these events can probably be linked to marine air masses that are normally associated with low DOC content (Willey et al., 2000) and high precipitation volume (i.e., dilution effect, see following section for the detailed discussion). With the aid of air mass back trajectory analyses, I excluded any extreme marine events, whose precipitation depths are greater than 90 mm, and obtained an average of 133 μM. It is slightly lower than that reported for terrestrial rain (VWA: 161 μM) on a global scale (Willey et al., 2000), and much higher than that observed at coastal

sites (Kieber et al., 2002). However, significantly higher values for DOC concentrations were found in precipitation over Northern China (VWA: 250 μM) (Pan et al., 2010), the closest continental region at the same latitude. This seems to be associated with its continental feature (i.e., neglectable marine inputs) and low annual precipitation amount (average of 635 mm in contrast with 1451 mm at Seoul). The monthly wet depositional fluxes of DOC were found to be high in summer and low in winter, with remarkable variations ranging from 0.24 to 4.04 μmol cm^{-2} $month^{-1}$ (Fig. 3.1b). The observed temporal trend can be largely attributed to the precipitation pattern rather than the source strength, as suggested by the significant positive correlation between monthly fluxes and precipitation amount ($r^2 = 0.78$, $p < 0.01$). The relatively low flux with respect to precipitation amount in September 2010 appears to be resulting from the excessive marine input in that month.

The DOC abundance in precipitation can be considered as a complex function of multiple controlling parameters. Besides the strength of the major sources (see next section), the storm origin effect on DOC concentrations has been the most frequently discussed in the literature (Kieber et al., 2002; Pan et al., 2010; Willey et al., 2006). According to air parcel backward trajectory regimes (72 h), all the events were categorized into three groups, as shown in Fig. 3.2. The first group (Type I) consists of events with air masses originating in Korea or adjacent coastal areas and thereafter remaining around the Korean peninsula. Owing to the relatively "stagnant" nature of these air masses, it is postulated that DOC in samples associated with these events was predominantly emitted by local sources within Korea. For Type II events, the air masses originated mostly from eastern

and northeastern China, and occasionally from Mongolia or Russia. They normally passed through the densely populated and industrialized areas of China, and subsequently entered Korea via the Yellow Sea or the East Sea. This type accounts for the largest fraction (47%) of events being investigated, implying the potentially significant contributions by emissions from China. The source areas for Type III events spreaded over the remote Pacific Ocean. These air masses spent a considerable amount of time traveling over the oceanic areas prior to making landfall on Korea. The VWA DOC concentration for Type I events was calculated to be 162 μM, which is the highest among all three groups. This high value can be largely linked to local continental sources, in which anthropogenic processes are expected to be dominant. Relatively lower values were found in other two groups, which were 111 μM for Type II and 62 μM for Type III, respectively. The precipitation events in these two groups presumably received considerable regional influences from long-range transport, which has been recognized to be a significant pathway of dispersion for air pollutants and other airborne species. The DOC in these samples is thus thought to be a mixture of organic substance derived locally and regionally from both continental and marine areas. Indeed, it has been suggested that Korea is subject to substantial influences by polluted air masses originating from China as well as clean marine air masses from the surrounding oceans (Kim et al., 2009). The lower concentrations for Type II events (in comparison with those of Type I) seem to be the result of the inclusion of marine air masses and/or the loss of the labile portion of organic matter during the transport. Likewise, the significantly higher values for the events associated with marine air masses (Type III) than that of “strictly” oceanic

rains (23 μM) (Willey et al., 2000) can thus be explained by the considerable contribution from local sources.

Furthermore, DOC in the atmosphere might vary with seasons, since biogenic emission from vegetation, as one of the major OC sources, is largely controlled by seasonality. As a result, relatively higher levels of DOC in rainwater have been found in warm (or growing) seasons in previous studies (Kieber et al., 2002; Willey et al., 2000). However, at this location, the reverse pattern was observed, for which winter precipitations were generally associated with higher DOC abundances (Fig. 3.1a). This phenomenon is likely due to the overwhelming anthropogenic contributions (in urban regions mostly fossil-fuel burning relevant processes lacking of temporal variations) which have rendered the seasonality of the natural biogenic fraction undiscernable (i.e., variations in biogenic input are not significant enough to impact the overall temporal pattern of DOC), as well as the low precipitation depth in the dry wintertime of this region. Similar seasonal variations have been documented in other areas where the anthropogenic contribution to rainwater DOC prevails (Pan et al., 2010).

In addition, the DOC concentration levels have been found to decrease with the increasing precipitation amount (Pan et al., 2010). However, the correlations between these two parameters are usually weak and can be absent occasionally, which has been attributed to continuous supplies of DOC during the process of precipitation (Kieber et al., 2002). The logarithmic regression analysis indicates DOC levels in the precipitation samples are largely controlled by dilution (Fig. 3.3), in such a manner that DOC is effectively “washed out” from the atmosphere by the initial precipitation (i.e. the DOC concentrations decrease with

precipitation amount) (Soyol-Erdene et al., 2011). The precipitation amount, therefore, is probably an important factor controlling DOC concentrations at this location, if taking into account the fact that the effect of any individual factor can be easily masked by those of others.

The dry period preceding the precipitation events might be another controlling factor, since the organic substances emitted locally may build up in the surface air and compose a large fraction of rainwater DOC through below-cloud scavenging. However, it was shown to be irrelevant to DOC levels in precipitation samples collected. Other potential controlling factors include storm type, wind speed, and the scavenging efficiency of precipitation (i.e. removal rate of airborne gases and particles by hydrometeors), which are beyond the scope of this study and thus are not discussed here. All the above parameters are not independent but interact with each other. The DOC abundance is therefore determined by the interplay among multiple controlling factors. Further studies encompassing all the potential parameters are thereby essential to elucidate the mechanism determining DOC concentration levels in wet deposition.

3.3.2. Sources of dissolved organic carbon in precipitation in Seoul

In general, biomass burning and fossil-fuel combustion were thought to be the most significant anthropogenic sources for rainwater OC, whereas biogenic emissions from both continental and marine areas may also contribute substantially. In this work, the source apportionment for DOC in precipitation was made by tracing the inputs from the potential sources using signature chemical species. The DOC concentrations were found to be correlated strongly with those

of nitrate and non-seasalt sulfate (Figs. 3.4a and b), the two widely used pollution indicators in atmospheric studies (Matsumoto and Uematsu, 2004). The positive relationships with one another among these species indicate their common origins — human activities. The gaseous precursors for nitrate and sulfate (i.e., NO_2 and SO_2) in Seoul and its neighboring areas have been reported to be emitted by industries, power plants, house heating, and vehicles (Chae et al., 2004). In particular, approximately 86% of SO_2 emissions were attributed to the first two sources in the province surrounding Seoul, which is thus expected to be a crucial source area. Since all the aforementioned processes utilize fossil-fuel as the energy source, it can be inferred that DOC in precipitation over Seoul is mainly derived from incomplete combustion of fossil-fuel.

I further employed vanadium, a reliable fingerprint for emissions from fossil-fuel combustion (Tsukuda et al., 2005), to justify my inference. A significant positive relationship was found between concentrations of DOC and non-crustal vanadium (Fig. 3.4c), indicative of fossil-fuel combustion as the dominant source for DOC. Fossil-fuels are primarily consumed by four major sectors: transportation, household heating, coal-/oil-firing electricity generation, and industrial production. The major fuels for ground transportation in the urban areas are gasoline and diesel; whereas house heating in winter season mainly consumes natural gas in Korea. Since the refining process removes most vanadium in fossil-fuels (Hope, 1997), it is unlikely that these two processes would be significant sources of vanadium content in the precipitation samples. On the other hand, the fuels consumed by power generation and industrial production are primarily crude oil and coal. In these raw materials and their fly ashes, vanadium was found to be

generally enriched (Tsukuda et al., 2005). In fact, these two anthropogenic processes are very likely to have significant impacts at this site. Seoul is a highly industrialized city with around 18,100 industrial factories occupying ca. 12% of the total area (Lee et al., 2005). The thermal plants (where coal and oil are fired) generate the largest portion (66.5%) of electricity annually in Korea. The majority (94%) of global fossil-fuel emissions takes place in the Northern Hemisphere (NH) (Cooke et al., 1999). Besides, Chung and Seinfeld (2002) suggested that primary organic aerosol was dominated by fossil-fuel emissions in Eastern Asia. Accordingly, DOC in rainwater derived from fossil-fuel is likely to surpass that from biomass burning and other sources in some NH urban regions. It is therefore concluded that the DOC observed in the precipitation over Seoul is produced predominantly by the combustion of crude fossil-fuels, especially during industrial production and power generation.

3.3.3. Magnitude of wet depositional DOC flux in Seoul and its implications

The annual wet depositional flux of DOC in Seoul was calculated to be 1.9 g C m^{-2} yr^{-1} (the sum of depositional amount per event), which falls within the range of those reported for continental and coastal rain DOC fluxes around the world (Willey et al., 2000). Moreover, it is identical to the 10-site-average value over Northern China (Pan et al., 2010). This value amounts to 1.2 Gg yr^{-1} over the entire Seoul area if assuming uniform deposition rate (calculated as depositional flux of 1.9 g C m^{-2} yr^{-1} times by the area of 605.36 km^2). Alternatively, the annual

flux of DOC in precipitation of Seoul can be calculated using the equation given below:

$$F_C = F_S \times R_{oxidation} \times f_w \times R_{C/S} \quad (1)$$

where F_C and F_S denote the wet depositional flux of DOC and emission influx of SO_2 to the atmosphere, respectively; $R_{oxidation}$ represents the conversion rate of sulfur dioxide to sulfate (64±18%) (Intergovernmental Panel on Climate Change (IPCC), 2001), whereas f_w indicates the fraction of sulfate subject to wet scavenging (83±6%) (IPCC, 2001); $R_{c/s}$ is the mass ratio between DOC and sulfur in the precipitation samples calculated from the linear regression slope in Fig. 3.4a (C/S = 1.3). Using the published official SO_2 emission data (2.8 Gg S yr^{-1}) (Environmental Statistics Yearbook 2010, http://eng.me.go.kr) would yield an annual wet depositional DOC flux of 1.9±0.6 Gg yr^{-1}. It is in general agreement with the value calculated above using the area, taking into account any potential variations of deposition rate of DOC within Seoul from the sampling location. Similar carbon to sulfur ratios for wet deposition were found in several other locations under significant anthropogenic influences, including South China (C/S = 1.7, 22.6 °N, 113.9 °E, 2005-2009) (Huang et al., 2010), The Netherlands (C/S = 1.4, 51.5 °N, 4.1 °E, 1980-1986) (Nguyen et al., 1990), Puerto Rico (C/S = 1.3, 51.5 ° N, 18.3 ° E, anthropogenic plume, 2004-2007) (Gioda et al., 2011). The organic matter to sulfate mass ratios in tropospheric aerosols at low altitudes (0.5-1.5 km column) in urban regions were found to be around 1 by aircraft measurements (Heald et al., 2005). If an organic-mass-to-organic-carbon ratio of 1.4–2.2 is taken (Aiken et al., 2008), the C/S ratio for these aerosols is thus calculated to be 1.4–2.1, which is consistent with those found in precipitation

samples. Furthermore, fossil-fuel combustion has been recognized to be the predominant source for global SO_2 emission (Lee et al., 2011). Therefore, by assuming that the DOC to sulfur ratio does not vary dramatically in precipitation over the regions where fossil-fuel combustion has significant impacts, one can extrapolate the above approximation to the global level. Given the global annual land surface anthropogenic SO_2 emission of 52 Tg S (Lee et al., 2011), approximately 36 ± 10 Tg DOC scavenged by wet deposition is generated from man-made processes (mainly fossil-fuel combustion) each year (Eq. 1).

Using the DOC flux in global continental rain of 340 ± 120 Tg per year (Willey et al., 2000) and the fossil-fuel DOC content in rainwater (Avery et al., 2006; Raymond, 2005) yields an annual net removal of 85 ± 35 Tg fossil-fuel derived DOC by precipitation, which is approximately twice of my estimate. However, the estimation of global flux by Willey et al. (2000) was made on the basis of measurements conducted over a decade ago. Rainwater DOC might have undergone considerable variations since that time, as being observed in the continental USA (Willey et al., 2006) and Southwestern China (Xu et al., 2009). In fact, the global atmospheric depositional flux of fossil OC has not yet been explicitly reported. OC scavenged by precipitation is thought to consist of both aerosols (POC and SOC) and gases (VOC). However, due to the limitation of methodology (HTCO), I actually analyzed non-purgeable DOC in the precipitation samples (Avery et al., 2009). It is assumed that VOC is completely removed during the initial step of this widely employed method and thus not quantified in rainwater DOC measurements. I tabulated the flux estimates of production of organic aerosols in the most recent works as Table 3.1. The best

estimates for POC and SOC subject to atmospheric scavenging were taken to be 10 ± 6 Tg and 7 ± 3 Tg, respectively. Taking into account in-situ oxidation, wet scavenging efficiency, and solubility, global wet depositional fossil-fuel DOC is calculated to be 12 ± 6 Tg (see the footnote of Table 3.1 for calculation). It is approximately one third of my estimate, and one seventh of that determined from global DOC rainwater flux and carbon isotopic ratios. These remarkable discrepancies signify the imperativeness of conducting further studies to reduce the uncertainties associated with the wet depositional flux of fossil-fuel derived DOC.

The fossil-fuel derived DOC flux based on my calculation, on an annual basis, is equivalent in magnitude to 8% of the global rainwater DOC flux reached by Willey et al. (2000) or 15% of the wet depositional OC to the global oceans estimated by Jurado et al. (2008). If compared with inorganic carbon, this figure is less than 1% of global annual CO_2 influx to the atmosphere from fossil-fuel burning, or less than 5% of the missing carbon sink in current global carbon cycling models (Schimel et al., 1996). This component of atmospheric OC, although not quantitatively significant in the global carbon budget, may take part in the regional carbon cycle and cause a variety of health and environmental problems. For example, organic aerosols are able to scatter and reflect solar radiation (direct effect) and influence cloud albedo (indirect effect), thereby altering the radiative balance of the atmosphere. Fossil-fuel derived organic aerosols (17 ± 9 Tg) (Table 3.1) correspond to a global atmospheric burden of 0.34 ± 0.18 Tg (Chung and Seinfeld, 2002). It could exert a top-of-the-atmosphere direct radiative forcing of -0.02 to -0.05 W m^{-2}, using the value of -36 to -76 W g

OC^{-1} (Chung and Seinfeld, 2002); or alternatively, -0.05 to -0.07 W m^{-2} (depending on the fraction of SOC), assuming that the direct radiative effect of organic aerosol is proportional to its burden (Maria et al., 2004). In addition, fossil-fuel combustion represents a significant source for the toxic organic constituents present ubiquitously in the atmosphere, such as polycyclic aromatic hydrocarbons (PAHs) (Qiao et al., 2006), which are considered to be highly mutagenic and carcinogenic. As such, fossil-fuel combustion derived atmospheric OC in urban areas may have profound implications on the environment and human health. Our magnitude estimation could contribute to the quantitative assessment on its impacts in various relevant fields.

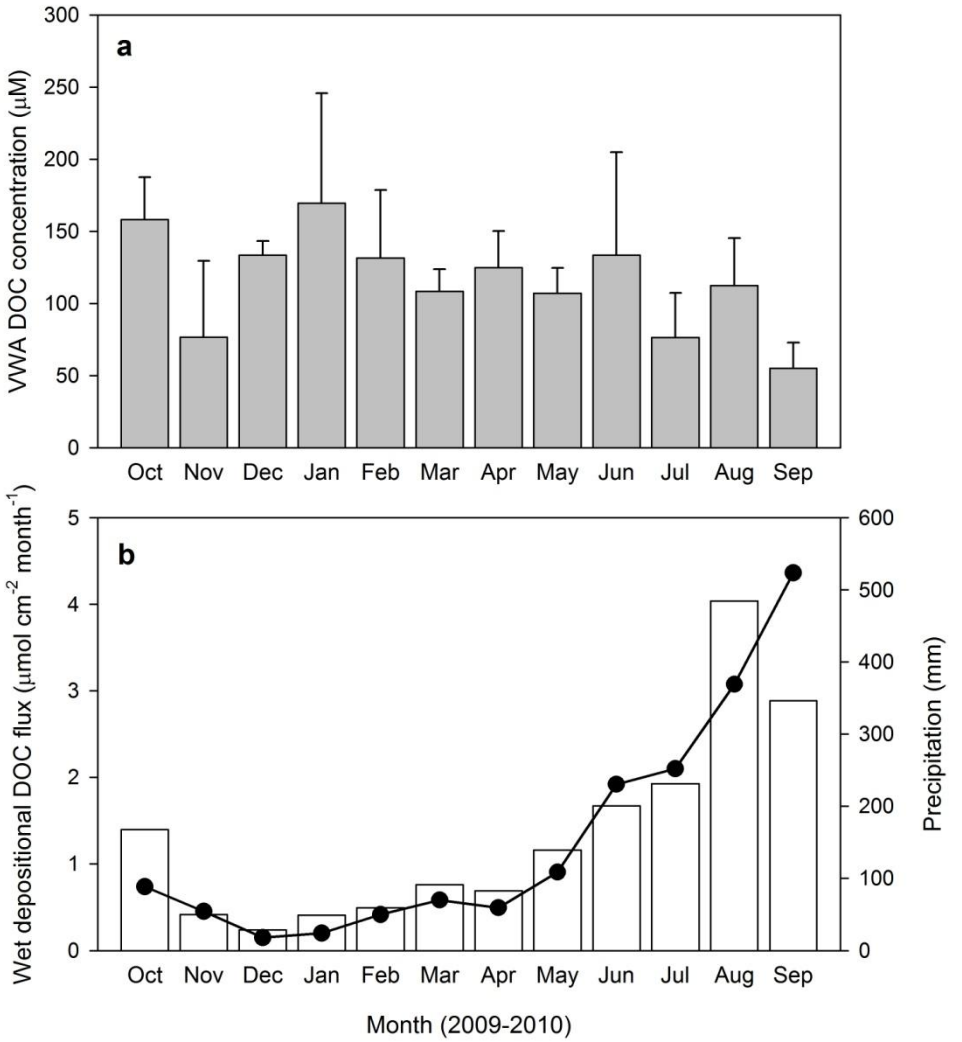
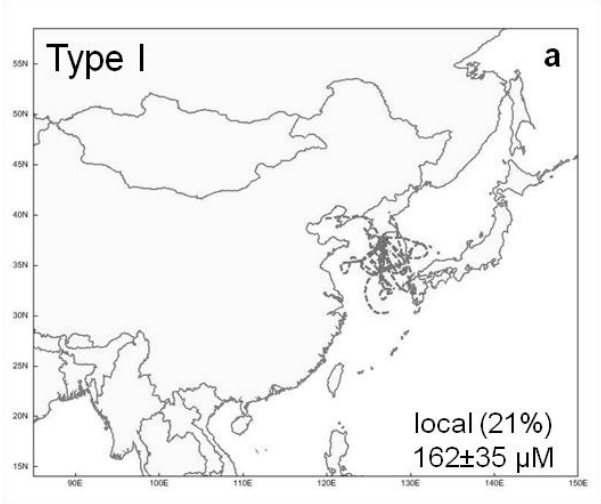
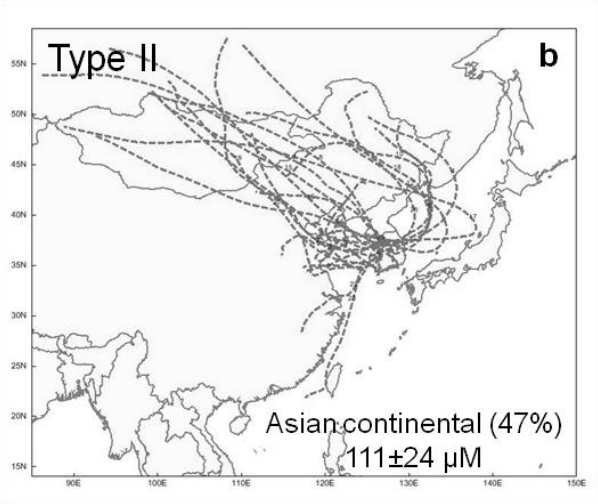


Figure 3.1. Temporal variations of DOC abundance levels in precipitation: (a) volume-weighted average concentrations and (b) integrated wet depositional fluxes and precipitation amount for each month during the sampling period from 2009 to 2010.





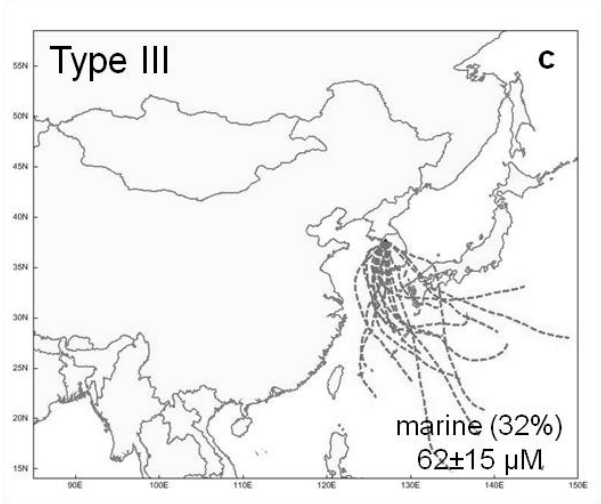


Figure 3.2. 72 h HYSPLIT air mass backward trajectories for precipitation in Seoul during 2009–2010. The precipitation events are categorized to three regimes: local (a), Asian continental (b), and marine (c). The frequency (expressed as percentage of total number of events) and average concentrations (VWA ± SD) for each regime are also shown.

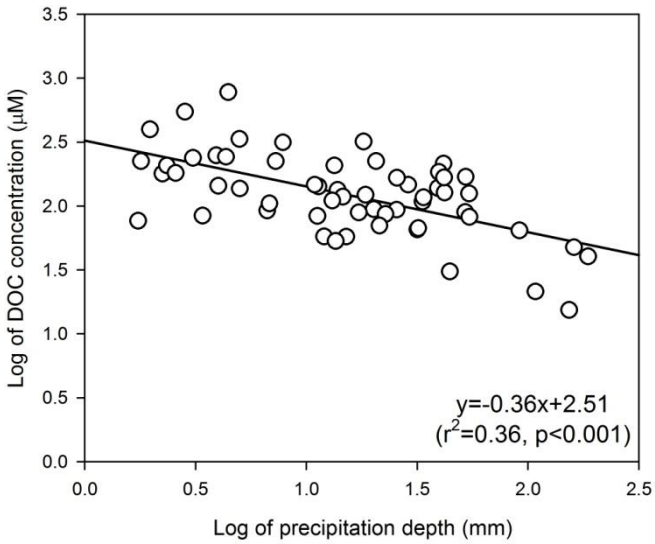


Figure 3.3. Concentrations of DOC versus precipitation depth for individual events observed in Seoul during 2009–2010.

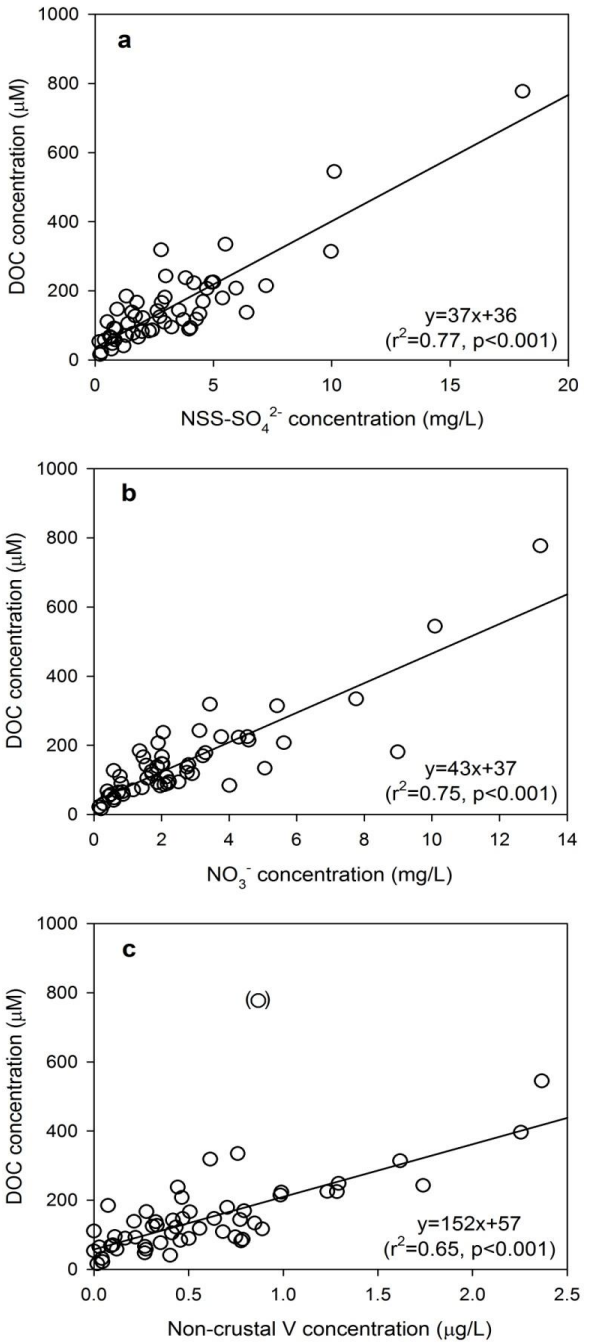


Figure 3.4. Plots showing correlations between concentrations of DOC and various source tracers: (a) non-sea-salt sulfate, (b) nitrate, and (c) non-crustal vanadium in individual precipitation samples collected in Seoul during 2009–2010.

Table 3.1. The magnitude of global wet depositional flux of fossil-fuel derived DOC and the production of fossil-fuel derived primary and secondary organic carbon in the aerosol phase.

Method	Flux (TgC/yr)	Reference
	DOC wet deposition	
Carbon isotope based	50-120	Avery et al., 2006; Raymond, 2005; Willey et al., 2000
Sulfate budget based	26-46	This study
Emission inventory based	6-18[a]	This study
	POC production	
	3-18	Hallquist et al., 2009
	5-15	Bond et al., 2004
	SOC production	
	1-9	Henze et al., 2008
	3-17	Hallquist et al., 2009
	6	Spracklen et al., 2011
	8	de Gouw and Jimenez, 2009

[a] The global flux of DOC in precipitation is calculated using the following equation:

$F_C = (P_{POC} + P_{SOC}) \times f_w \times f_{dis.}$

where F_C represents wet depositional flux of DOC; P_{POC} and P_{SOC} denote the productions of POC and SOC, respectively; f_w indicates the fraction of organic aerosol removed by wet deposition (80±5% of total wet plus dry) (Kanakidou et al., 2005); $f_{dis.}$ signifies the percentage of rainwater organic carbon accounted for by dissolved phase (85±5%, Pan et al., 2010, Willey et al., 2000). Oxidation of organic aerosol (POC and SOC) to CO/CO_2 is assumed to be neglectable (Hallquist et al., 2009).

4. Dissolved total hydrolyzable enantiomeric amino acids in precipitation: Implications on bacterial contributions to atmospheric organic matter

4.1. Introduction

Organic matter (OM) plays a significant role in the biogeochemical cycling of bio-reactive elements, especially carbon and nitrogen. While a labile fraction of OM is readily decomposed through microbially or photochemically mediated processes and remineralized to inorganic carbon and mineral nutrients, a considerable portion of OM (refractory) is relatively resistant to degradation and can persist in the natural environment for millennia, as in the case of marine dissolved OM (DOM) (Nagata, 2000; Carlson, 2002). Although it is well known that the bioavailability of OM is closely linked to its chemical identity, OM in terrestrial, aquatic, and atmospheric environments remains largely uncharacterized at the molecular level (Hedges et al., 2000; Goldstein and Galbally, 2007), which greatly hinders our understanding of its origins and reaction potential. A consensus has recently been reached on the significance of bacterial activity in shaping OM quantity and quality through its substantial contributions to production, transformation and consumption of OM (Tremblay and Benner, 2006, 2009; Mou et al., 2008; Jiao et al., 2010).

A fraction of OM resides in the atmosphere and has increasingly been recognized to constitute a significant part of global biogeochemical cycles and nutrient budgets (Cornell et al., 1995; Willey et al., 2000; Duce et al., 2008; Jurado et al., 2008; Cape et al., 2011; Cornell, 2011; Kanakidou et al., 2012;). The

vast majority of atmospheric OM is removed through wet and dry deposition and ultimately returns to the Earth's surface (Hallquist et al., 2009), where it is subject to degradation and preservation processes. However, due to the limited knowledge on its composition, little is known about the bioavailability of this atmospheric OM (Avery Jr. et al., 2003; Duce et al., 2008; Kanakidou et al., 2012), resulting in large uncertainties in our understanding of its fate and biogeochemical role in the receiving ecosystems.

One of the most important compound classes that comprise atmospheric OM are amino acids, which are primarily derived from biological origins in terrestrial and marine ecosystems (Ge et al., 2011 and references therein). Owing to their low-volatile nature, amino acids in the atmosphere have been identified mainly in condensed phases by previous workers, such as aerosols, rainwater, fog droplets and dew water (Scheller, 2001; Zhang and Anastasio, 2001; Kieber et al., 2005; Mandalakis et al., 2011). Despite the growing number of studies being conducted on atmospheric amino acids worldwide, few of them deal with combined amino acids (e.g., peptide and protein), which is, however, the dominant form for amino acids present in most environments. It has been found that in the atmosphere, the concentrations of amino acids residing in combined form are generally 4 to 5 times higher than those in free form (Scheller, 2001; Zhang and Anastasio, 2003; Wedyan and Preston, 2008; Mandalakis et al., 2011; Samy et al., 2013). Moreover, to my knowledge, the enantiomeric isomers (L and D) of atmospheric amino acids have been scarcely investigated, except for two studies on marine aerosols by Kuznetsova et al. (2005) and Wedyan and Preston (2008). Since the D-isomers of amino acids occur almost exclusively in bacteria and particularly in the cell wall

biopolymer peptidoglycan (Schleifer and Kandler, 1972; Benner and Kaiser, 2003; Kaiser and Benner, 2008), they can be used as biomarkers to trace and evaluate bacterial contributions to organic matter pool in natural environments (McCarthy et al., 1998, Kaiser and Benner, 2008).

Indeed, there is an increasing number of studies demonstrating the substantial contributions from bacteria to the OM pool in various aquatic environments, including marine waters and sediments (McCarthy et al., 1998; Dittmar et al., 2001; Ogawa et al., 2001; Perez et al., 2003; Kaiser and Benner, 2008, 2012; Kawasaki et al., 2011), freshwaters (Tremblay and Benner, 2009; Carstens et al., 2012; Kawasaki et al., 2013), and estuaries (Bourgoin and Tremblay, 2010; Fernandes, 2011). In view of the significance of bacterially derived OM in these aquatic systems, and the well-known presence of bacterial activity in the atmosphere (Sattler et al., 2001; Burrows et al., 2009; Va ïilingom et al., 2012), we may expect noteworthy bacterial contributions to atmospheric OM, which have, however, not been evaluated yet. In addition to the bacterial imprint, OM is usually characterized by using various qualitative indicators, such as carbon to nitrogen atomic ratios and amino acids yields (Davis et al., 2009; Tsukasaki and Tanoue, 2010). Nevertheless, the sources, compositions, and transformation pathways of OM in the atmosphere are highly complex and significantly different from those in other environments. OM emitted as aerosols (primary organic aerosol) into the atmosphere is mostly derived from incomplete combustion processes (i.e., fossil-fuel and biomass burning), whereas OM from biogenic sources (i.e., produced by modern plants and animals in terrestrial and aquatic systems) enters the atmosphere primarily in the gaseous phase, a fraction of which

is subsequently converted to aerosols (secondary organic aerosol) (Hallquist et al., 2009). As a result, the bacterial degradation processes can take place in the surface ecosystems before the OM is emitted, as well as on the aerosols in the air and in the cloud water (Amato et al., 2007; Husárová et al., 2011) after the emission. The latter process probably occurs on a relatively short time scale, considering residence time of aerosols in the troposphere (Balkanski et al., 1993; Papastefanou, 2006). Therefore, it is generally believed that OM in the atmosphere is mainly subject to abiotic photochemical aging processes and the biological degradation is less important, although the in-situ biodegradation of OM in the atmosphere has rarely been evaluated.

In the present work, I sought to improve our understanding of OM in the atmosphere from the biogeochemical perspective by investigating precipitation samples. Total hydrolyzable enantiomeric amino acids along with the bulk parameters (i.e., carbon and nitrogen) were analyzed to examine the distributions and characteristics of OM in the dissolved fraction. In addition, the contributions from bacteria to DOM in precipitation were explored using D-amino acids as bacterial biomarkers.

4.2. Study site and sample collection

Taking into account the geographical features of Korea (i.e., a peninsula), two sites with contrasting environmental settings and anthropogenic influence levels were selected as representatives: Seoul (an inland urban area with large terrestrial input) and Uljin (a coastal rural area with large marine input). Seoul (37.5°N, 127°E) is a typical Asian metropolis situated in the midwestern part of the Korean

peninsula, of which a detailed description has been given in Chapter 3. The other sampling site, Uljin (37 °N, 129.4 °E), is located on the eastern coastline of Korea and has a small population of around 52,000 inhabiting an area of 989.06 km^2. Its proximity to the East/Japan Sea and weak human impacts render it an area characterized by a relatively pristine atmospheric environment, which I have employed as a reference for the Seoul study in terms of marine contribution and anthropogenic impact.

The sampling campaigns were carried out on a four-storey building rooftop at the Gwanak campus of Seoul National University in Seoul from March 2012 to February 2013, and on the roof of a research facility at Korean Institute of Ocean Science and Technology in Uljin from February 2011 to January 2012, respectively. Rainwater was collected on an event basis using a home-made sampler, which consists of a polypropylene funnel (dia. 250 mm) joined to a high-density polyethylene (HDPE) bottle placed in a covered bucket through Tygon FEP-lined tubing. This apparatus was thoroughly cleaned with dilute acid, and manually deployed prior to onset of precipitation and retrieved after cessation. Depending on the intensity of precipitation, the sample volumes ranged from 60 mL to 5000 mL. The sampling duration was typically less than 24 h and can be more than 48 h for rainstorms in summer. The contributions to the precipitation samples from dry deposition were minimized by strictly controlling the exposure time to dry conditions (no more than 5 h for overnight events and less than 1 h for the rest). In a laminar flow clean room, the samples were filtered through Whatman 0.7 μm GF/F glass fiber filters (pre-combusted at 500 °C). Subsamples for quantification of dissolved organic carbon (DOC) and amino acids were

transferred to 20 mL pre-muffled glass ampoules (5 h at 500 ℃), followed by chemical preservation with 6 M pure hydrochloric acid (HCl) and fire sealing using a hand-held butane burner. Aliquots for quantification of dissolved organic nitrogen (DON) were placed in pre-cleaned HDPE bottles and kept frozen at –20 ℃ until analysis.

4.3. Results and Discussion

4.3.1. Distributions and characteristics of DOM in precipitation

4.3.1.1. Abundances and variations of DOM in precipitation

The DOM in precipitation collected in this study was characterized by analysis of the major bioelements—carbon and nitrogen. The concentrations of DOC and DON ranged from 24 to 433 μmol L^{-1} for DOC and from below detection limit (BD) to 91 μmol L^{-1} for DON at Seoul, and from 9 to 849 μmol L^{-1} for DOC and from BD to 145 μmol L^{-1} for DON at Uljin, respectively (Table 4.1). The volume-weighted average (VWA) (Topol et al., 1985) concentrations were found to be higher at Uljin than at Seoul for both DOC and DON. This may not necessarily imply that the source strength for OM is stronger at Uljin. Instead, the observed pattern can be partially attributed to the difference in annual precipitation amount (1600 mm at Seoul vs. 1280 mm at Uljin), since precipitation amount could exert a significant influence on the abundance of wet depositional species.

The concentration levels of DOC and DON in precipitation showed remarkable seasonal variations at both sites (Fig. 4.1), with relatively high values being observed in spring, early summer, and fall. The temporal trends for DOC

and DON were generally in agreement at Uljin, whereas significant discrepancies were found in variation patterns between DOC and DON at Seoul. It seems that in comparison with Seoul, the production and scavenging processes of DOC and DON at Uljin were more consistent. Since DOC in precipitation in Seoul has been suggested to be primarily controlled by human activities (i.e., fossil-fuel combustion) (Yan and Kim, 2012), it is likely that DON is subject to more contributions from natural/biological sources. Moreover, taking into account the remoteness of Uljin, it is inferred that biogenic sources play a more important role in the production of atmospheric OM at this location. These speculations were supported by the correlations of DOC and DON with nitrate, which is generally considered to be derived from anthropogenic sources (mainly fossil-fuel combustion) and widely used as a pollution indicator in atmospheric studies (Matsumoto and Uematsu, 2005). The randomly distributed data points in the scatter plot (Fig. 4.2A) of DON against nitrate suggest DON in precipitation at both locations stems from sources independent of those for nitrate, and is presumably of biological origin. However, a significant positive relationship was found between DOC and nitrate in Seoul (Fig. 4.2B), indicative of anthropogenic origins for DOC. The positive yet less significant correlation observed for DOC at Uljin might be the result of substantial influences from inland polluted areas by long-range transport, owing to the downwind location of Uljin (the prevailing wind systems for Korea are westerlies).

The DOM in the precipitation samples was further characterized at a molecular level by investigation of a specific organic compound class—amino acids. Concentrations of THAA ranged from 23 to 804 nmol L^{-1} (VWA = 117

nmol L^{-1}) at Seoul and from 34 to 4250 nmol L^{-1} (VWA = 384 nmol L^{-1}) at Uljin (Table 4.1). The average molar compositions of the THAA pool were very similar at the two sampling locations (Fig. 4.3). Glycine (Gly) was shown to be the most abundant species, contributing approximately 30% of the THAA pool in the precipitation. Other dominant individual amino acids include alanine (Ala), aspartic acid (Asp), glutamic acid (Glu), and serine (Ser), which are normally found to be significant contributors to amino acids pool in aquatic environments. The relative distributions of these amino acids are in general accordance with those observed in the atmospheric environments at other locations, where similar dominant species were present (Scheller, 2001; Mandalakis et al., 2011). It is worth noting that glycine and amino butyric acid (GABA) were more abundant at Seoul than at Uljin, implying the amino acids were on the whole more degraded at Seoul, since these two species are generally considered to be relatively refractory individual amino acids (Yamashita and Tanoue, 2003; Davis et al., 2009). Nevertheless, the source variations may also contribute to the distribution patterns of GABA observed here, since eukaryotic organisms and bacteria are known to synthesize free GABA (Koolman and Roehm, 2005). Rather similar temporal trends were observed for THAA concentrations at Seoul and Uljin (Fig. 4.4), with higher values occurring in spring and fall and lower values in summer, which can be ascribed to the variations of input source strength as well as the precipitation pattern of Korea (i.e., extraordinarily high in summer).

4.3.1.2. Qualitative characterization of DOM in precipitation

The overall bioavailability of OM can be evaluated by several methods, such as direct assessments by conducting incubation experiments and indirect speculations using various qualitative indicators of OM. One of the most widely used indicators is the carbon to nitrogen atomic ratio (C/N) of OM (Vandewiele et al., 2009; Tsukasaki and Tanoue, 2010), since nitrogen is thought to be the biologically limiting nutrient. The average C/N ratios were calculated to be 29 (median = 15) and 11 (median = 8) for DOM in precipitation from Seoul and Uljin, respectively (Fig. 4.5A). These values were found to be comparable to those reported for aerosols elsewhere (Aiken et al., 2009; Sun et al., 2009; Lin et al., 2010), which span a wide range from 10 to 100. The C/N ratios for phytoplankton and bacteria were shown to be varying from 4 to 8, while terrestrial OM has ratios between 12 and 200 (Lee and Fuhrman, 1987; Hedges and Man, 1979). During the biodegradation, the C/N ratios of marine OM normally increase due to the preferential utilization of N-rich components (Libes, 1992). By contrast, terrestrial OM usually has high C/N ratios (e.g., plant tissues) which decrease as the decomposition proceeds, due to the incorporation of bacterial detrital biomass (enriched in N) into residual OM (Tremblay and Benner, 2006). The variations in these ratios, which reflect the compositional changes of OM pool resulting from diagenetic alterations as well as changes in contributing sources, are thus usually used to evaluate the bioreactivity and to speculate the sources of natural OM. The relatively high C/N ratios observed at Seoul might be attributed to a higher content of C-rich OM derived from anthropogenic origins (e.g., hydrocarbon-like organic aerosol) (Aiken et al., 2009), and probably, to a lesser extent, to higher

contributions from terrestrial sources (e.g., soil). The lower C/N ratios at Uljin suggest atmospheric OM at this remote location, which is subject to low human impacts and high contributions from marine sources, might possess a higher value as substrates for microbial utilization after deposition to the surface ecosystem.

In addition, the diagenetic state of OM is frequently characterized by quantification of amino acids, which are ubiquitous constituents of terrestrial and aquatic organisms and represent a significant fraction of living and detrital OM (Cowie and Hedges, 1992). Diagenetic indicators have been developed based on the relative abundance and molar composition of amino acids (Cowie and Hedges, 1994; Dauwe and Middleburg, 1998; Davis et al., 2009): carbon- or nitrogen-normalized yields of amino acids (THAA-C% or THAA-N%), which generally tend to decrease during diagenesis in the marine environment (an opposite trend was found for terrigenous OM (Tremblay and Benner, 2006)); the relative abundance of non-protein amino acids, which has been shown to increase as the degradation progresses; and the degradation index (DI) developed based on compositional changes of amino acids pool, for which higher values indicate the OM is relatively "fresh". It is found that THAA represented on average 0.7% of DOC (median = 0.6%) and 3.8% of DON (median = 2.7%) at Seoul, and 1.8% of DOC (median = 1.4%) and 6.0% of DON (median = 2.1%) at Uljin, respectively (Fig. 4.5B). The average ratios of Glu to its non-protein degradation product GABA (Glu/GABA) were calculated to be 3.5 (from 1.0 to 10.9) and 7.9 (from 3.2 to 31.8) at Seoul and Uljin, respectively (Fig. 4.5C). For calculation of DI, I did not use the coefficients given in any previous reference dataset (Dauwe et al., 1999; Yamashita and Tanoue., 2003; Davis et al., 2009), which were intended for

OM in the marine environment and may not be applicable in this study. Instead, the DI was calculated as the first principal component score from principal component analysis (PCA) applied to my own dataset (including all the individual amino acids analyzed except GABA) following the method described by Dauwe et al. (1999). Since this dataset did not cover the entire possible range of degradation states in atmospheric amino acids, the values obtained here are only for comparisons among samples within this study. The calculated DIs ranged from –1.8 to 1.0 (average of –0.5) and from –1.0 to 2.2 (average of 0.6) for Seoul and Uljin, respectively (Fig. 4.5D).

The variation patterns of these indicators were further compared through correlation analyses conducted on the entire data set (Seoul and Uljin). While a good correlation was found between DIs and Glu/GABA (Fig. 4.6A), it appears that THAA-C%, THAA-N% and C/N were not well related to the indicators calculated based on amino acid compositions (Figs. 4.6B, 4.6C and 4.6D). This might de due to the inconsistent behaviors of these qualitative indicators (i.e., those related to C or N content) in terrestrial and marine environments, since OM in my samples was probably derived from both environments. Besides, the diagenetic history of amino acids might be decoupled from that of bulk OM in the atmosphere, taking into account their potentially independent sources. Nevertheless, DI and Glu/GABA seem to consistently indicate that amino acids in precipitation at Uljin were at a relatively early diagenetic stage compared with that at Seoul, though source variations may also contribute to the observed pattern. Accordingly, these widely used indicators are probably not appropriate for evaluating the diagenetic state of atmospheric OM, although some of them (i.e.,

those solely derived from amino acids) may still be useful for investigation of the diagenesis of amino acids. In addition, no correlations were found among indicators obtained based on bulk parameters (C/N, THAA-C%, and THAA-N%) (data not shown), suggesting variations of these indicators might reflect changes in compositions of DOM resulting mainly from varying contributing sources. This may imply that in-situ bacterial degradation only plays a minor role in shaping the OM in the atmosphere.

The photochemical oxidation processes might also contribute to the compositional changes of OM in the atmosphere. However, I did not expect that atmospheric OM at either one of these sites underwent particularly more photochemical degradation than at the other. It is therefore unlikely that this process exerts a major influence on the discrepancies in DOM composition observed. Since amino acids are generally thought to be of biological origin, the larger fraction of DOM accounted for as amino acids (i.e., THAA-C% and THAA-N%) observed at Uljin can be attributed to the higher contribution from biological sources to atmospheric OM in this region. In addition, the bulk chemical properties of DOM (e.g., C/N ratios and amino acids yields) at Uljin better resemble those of natural DOM in the aquatic systems (Maie et al., 2006 and references therein) compared with Seoul, which further confirms my inference that the atmospheric OM at Uljin was subject to more contributions from biological sources. Overall, it appears that OM in the atmosphere derived from natural/biological origins at remote locations (e.g., Uljin) bears a higher potential biogeochemical reactivity than that from urban/polluted areas (e.g., Seoul).

4.3.2. D-amino acids and bacterial signature in DOM in precipitation

Four D-enantiomers of amino acids (D-Asp, D-Glu, D-Ser, and D-Ala) were ubiquitously present in all the samples from both Seoul and Uljin, with D-Ala as the most abundant species. Other D-amino acids such as D-phenylalanine and D-leucine were occasionally found in some samples and were only present at negligible levels. The enantiomeric ratios (D/L) ranged from 0.09 to 0.65 for Asp, 0.05 to 0.56 for Glu, 0.02 to 0.83 for Ser, and 0.24 to 0.93 for Ala at Seoul, and from 0.08 to 0.38 for Asp, 0.04 to 0.40 for Glu, 0.02 to 0.38 for Ser, and 0.08 to 0.62 for Ala at Uljin, respectively. The variations of D/L ratios of these amino acids were in good agreement (Table 4.2), suggesting similar origins for the D-enantiomers. The relatively weak correlations between D/L ratios of Ser and those of other three amino acids might be due to the differences in source bacteria. In general, these D/L ratios showed small seasonal variations at both Seoul and Uljin (Figs. 4.7 and 4.8). The summer values at Seoul were shown to be slightly lower for Asp, Glu, and Ala yet relatively higher for Ser (Fig. 4.7), which is probably linked with the elevated input of amino acids from marine sources at this time of year (see discussion in the following). However, this pattern was not observed at Uljin (Fig. 4.8), which can be explained by the close proximity of the sampling site to the ocean (i.e., the enhanced marine contribution in summer was indiscernible).

The average D/L ratios of Asp, Glu, Ser, and Ala were 0.34, 0.26, 0.21, and 0.61 respectively for Seoul, and 0.18, 0.11, 0.09, and 0.31 respectively for Uljin (Fig. 4.9). By comparison, the average D/L ratios were reported to be 0.10 (0.07–0.15) for Asp, 0.05 (0.01–0.07) for Glu, 0.05 (0.02–0.13) for Ser, and 0.08 (0.04–

0.16) for Ala of total (both water-soluble and insoluble) amino acids in aerosols collected in the central Ligurian Sea and Long Island Sound, USA by Kuznetsova et al. (2005). They also suggested that bacterial signature is much stronger in dissolved than in particulate amino acids. Therefore, these significantly lower D/L ratios than those observed in this study might be attributed to the inclusion of the water-insoluble (or particulate) amino acids which are characterized by low enantiomeric ratios (Kuznetsova et al., 2005 and references therein). In another study on aerosols collected over the remote Atlantic Ocean, D/L ratios for Ala and Ser were found to be 0.35 and 0.11 on average for water-soluble amino acids (Wedyan and Preston, 2008), which are lower than those at Seoul but similar to those at Uljin. It seems that on the whole the D/L ratios of amino acids at Uljin better resemble those obtained from marine aerosols, which is consistent with the marine feature of Uljin.

The distribution patterns of these four D-amino acids were remarkably consistent for Seoul and Uljin (Fig. 4.9), which may suggest their similar origins at both sites. Interestingly, the characteristic enantiomeric pattern observed here was also found for the D-enantiomers of dissolved total amino acids in aquatic systems (Dittmar et al., 2001; Perez et al., 2003; Kaiser and Benner, 2008), where D-amino acids were suggested be derived from bacterial sources. In addition to bacteria, some archaea were reported to contain D-amino acids, which are characterized by significantly lower (more than one order of magnitude) D/L ratios than those found in bacteria and the precipitation samples. Besides, distinct enantiomeric patterns were observed in archaeal cell material, in which Ala has the lowest D/L ratios in comparison with Asp, Glu, and Ser (Nagata et al., 1998,

1999; Matsumoto et al., 1999). Moreover, the aging processes (natural chemical racemization) may convert L-enantiomers of amino acids to the corresponding D-amino acids. However, the contribution from this source is of importance only over geological timescales (approximately 10^4 to 10^6 yrs at 0 ℃) (Bada, 1982) and is generally neglected, as in previous studies. Therefore, the D-amino acids observed in the precipitation samples can be primarily attributed to bacterial production.

It is noteworthy that the enantiomeric ratios for samples collected at Seoul were significantly higher than those at Uljin. Laboratory experiments have shown that D-amino acids, bacterial biomolecules (e.g., peptidoglycan), and bacterial DOM are more resistant to biodegradation than algal DOM and protein (Jørgensen et al., 1999, 2003; Amon et al., 2001; Nagata et al., 2003), thus D-amino acids could build up during diagenesis and the corresponding D/L ratios can be used as degradation indicators. In addition, the D/L ratios in terrigenous OM (e.g., plant detritus) were also found to increase during microbial decomposition (Tremblay and Benner, 2006). Therefore, my results may suggest amino acids in the atmospheric environment of Seoul were more intensively reworked by bacteria than those at Uljin, though productions of D-amino acids by other processes (see discussion above) may also contribute to the high D/L ratios observed at Seoul. In addition, this pattern is in accordance with those of other amino acid-based diagenetic indicators (i.e., Glu/GABA and DI), confirming the significant impacts of bacterial degradation on amino acids composition in the precipitation samples. Since the terrigenous OM is thought to be more refractory than its marine counterpart (Hedges et al., 1997; Burdige, 2005), it is likely that

amino acids derived from terrestrial environments are on the whole more degraded than those from marine ecosystems. The observed distributions of D/L ratios thus seem to be associated with the relatively higher contributions from terrestrial sources to atmospheric amino acids at Seoul than at Uljin. Nevertheless, my speculation on different reactivities of amino acids in terrestrial and marine environments are not supported by any direct evidences, and further study on this regard is thereby warranted. Moreover, as being discussed previously, the inferred diagenetic states of amino acids are independent of the bulk DOM, and presumably to a large extent reflect the initial diagenetic status of amino acids before they were emitted into the atmosphere.

Alternatively, the discrepancy in enantiomeric ratios for atmospheric amino acids from the two study sites may be attributed to the difference in the composition of the bacterial communities. It is very likely that in addition to bacteria inhabiting the terrestrial matrices (e.g., soil), marine bacteria also contribute to D-amino acids in the precipitation samples through sea-air interactions (Burrows et al., 2009). The inland transport of marine microbes via atmosphere has been demonstrated in previous microbiological studies (Ahern et al., 2007; Dueker et al., 2012b). In particular, marine bacteria were identified in rainwater collected in 2011 at Seoul by Cho and Jang (2014). Due to the close proximity of Uljin to the East/Japan Sea, we may expect more contributions from marine bacteria to atmospheric amino acids at Uljin compared with Seoul. It has been found that while the aquatic systems are predominated by Gram-negative bacteria (Moriarty and Hayward, 1982; Giovannoni and Rappe, 2000; Jørgensen et al., 2003), Gram-positive bacteria can be comparatively more important in the

terrestrial environment (Janssen, 2006; Lauber et al., 2009). Indeed, Gram-negative bacteria were shown to comprise 83% of bacterial isolates from marine aerosols over the East/Japan Sea (Cho and Hwang, 2011). On the contrary, Gram-positive bacteria were found to be dominant (>75%) in aerosols collected at Newton Creek, located in a densely populated area of New York (Dueker et al., 2012a). However, several bacterial species with high abundances in rainwater at Seoul were Gram-negative (the contribution was not given) (Cho and Jang, 2014). This might be attributed to the significant impacts of marine air masses on precipitations at Seoul during the sampling period (i.e., late spring and summer). In addition, owing to much thicker cell walls than in Gram-negative bacteria (Schleifer and Kandler, 1972; Madigan et al., 2000), Gram-positive bacteria in general have a higher content of D-amino acids (Jørgensen et al., 2003; Kaiser and Benner, 2008). Further, on the basis of air mass backward trajectory analyses (Fig. 4.10), I found the average D/L ratios (data not shown) for samples with a dominant contribution from terrestrial sources are higher than those with marine origins (except Ser). Consequently, it can be concluded that the relatively high enantiomeric ratios for Seoul samples might be indicative of an advanced diagenetic state of amino acids, whereas the potential impact of source bacterial community structure cannot be excluded.

4.3.3. Implications on bacterial contributions to organic matter in the atmosphere

Since D-amino acids are ubiquitously present in the precipitation samples, I expect a considerable contribution from bacterial cells and their remnants to DOM

pool in precipitation. In earlier studies, the bacterial signature in OM was mainly evaluated based on D-amino acids contained in peptidoglycan (McCarthy et al., 1998; Dittmar et al., 2001; Pedersen et al., 2001; Grutters et al., 2002; Perez et al., 2003; Jones et al., 2005; Lomstein et al., 2006). However, it has recently been suggested by Kaiser and Benner (2008) that, in addition to peptidoglycan, D-amino acids are derived from numerous other bacterial macromolecules (e.g., teichoic acid and lipopeptides). Furthermore, they proposed an approach for estimating bacterial contribution to OM by using the following equation:

$$\%\text{Bacterial C or N} = 100[\text{biomarker}]_{\text{sample}}/[\text{biomarker}]_{\text{bacteria, bacterial DOM}} \quad (1)$$

where $[\text{biomarker}]_{\text{sample}}$ and $[\text{biomarker}]_{\text{bacteria, bacterial DOM}}$ denote the C- or N-normalized yields of a specific biomarker (e.g., D-Ala) in sample OM and in cultured representative bacterial cells or freshly produced bacterial DOM (Kaiser and Benner, 2008).This approach has been frequently employed in subsequent studies and its reliability was validated by comparison of results obtained using multiple biomarkers and other independent approaches (Tremblay and Benner, 2006; Kaiser and Benner, 2008; Carstens et al., 2012).

However, it seems unlikely to achieve a quantitative assessment of bacterial contributions to DOM in the precipitation samples using this approach based on the limited information obtained in this study and literatures. Firstly, in comparison with aquatic environments, the atmosphere is a very dynamic system, which makes the determination of contributing bacterial community (presumably from both terrestrial and marine environments) compositions a big challenge. Secondly, considering the inherent complexity and diversity of bacterial communities (Burrows et al., 2009) that might contribute to atmospheric amino

acids, it is rather difficult to obtain representative end-member bacterial D-amino acid yields, particularly for the terrestrial systems, information on which is extremely limited. Nevertheless, C- and N-normalized yields of D-Ala (the most representative D-amino acid) in DOM of our samples (0.4–18 with a median of 5.8 nmol mg C^{-1} and 7.5–320 with a median of 84 nmol mg N^{-1} at Seoul, and 3.0–19 with a median of 7.3 nmol mg C^{-1} and 7.0–280 with a median of 52 nmol mg N^{-1} at Uljin) were found to be comparable to those in DOM from the North Pacific and North Atlantic Ocean (Kaiser and Benner, 2008), the Amazon River (Tremblay and Benner, 2009), the St. Lawrence Estuary (Canada) (Bourgoin and Tremblay, 2010), and the Kasumigaura Lake (Japan) (Kawasaki et al., 2013). The highly variable D-Ala yields observed in this study in comparison to those in aquatic systems can be linked with the dynamic nature of the atmospheric environment. The bacterial contributions were estimated to be 30 to 50% for lacustrine DOC (Kawasaki et al., 2013), and 20 to 30% and 40 to 60% for marine DOC and DON (Kaiser and Benner, 2008), respectively. Although I am not able to perform such quantitative estimation based on the information available, it is very likely that bacteria and their debris constitute up an important fraction of OM in the atmosphere.

After this bacterially derived atmospheric OM being deposited to the surface ecosystems, a considerable part is likely to escape remineralization and contribute to the sequestered organic carbon pool, since it has been suggested that bacterial transformation is an important mechanism for OM preservation (Ogawa et al., 2001; Tremblay and Benner, 2006; Jiao et al., 2010; Kaiser and Benner, 2012). Avery Jr. et al. (2003) found that the bioavailability of rainwater DOC is

significantly higher (approximately 6 times) than that of riverine DOC based on incubation experiments. Such a large discrepancy can be, at least partially, attributed to the difference between the relative proportions of bacterial C content of DOM in rainwater and rivers. On the other hand, the bacterially derived portion of atmospheric OM (especially N) may also contribute to the secondary productivity of the receiving ecosystems, since a substantial fraction of bacterial OM is considered to be bioavailable (Kaiser and Benner, 2008). As such, despite the insignificant role of bacterial degradation in OM in the atmosphere, the overall bioreactivity of atmospheric OM could be influenced by the relative contribution from bacteria. Therefore, it is imperative to conduct more intensive studies to provide a quantitative constraint on the bacterial contribution to atmospheric OM, taking into account the potential impacts of bacteria on the post-depositional fate of OM in the atmosphere as being discussed in this work.

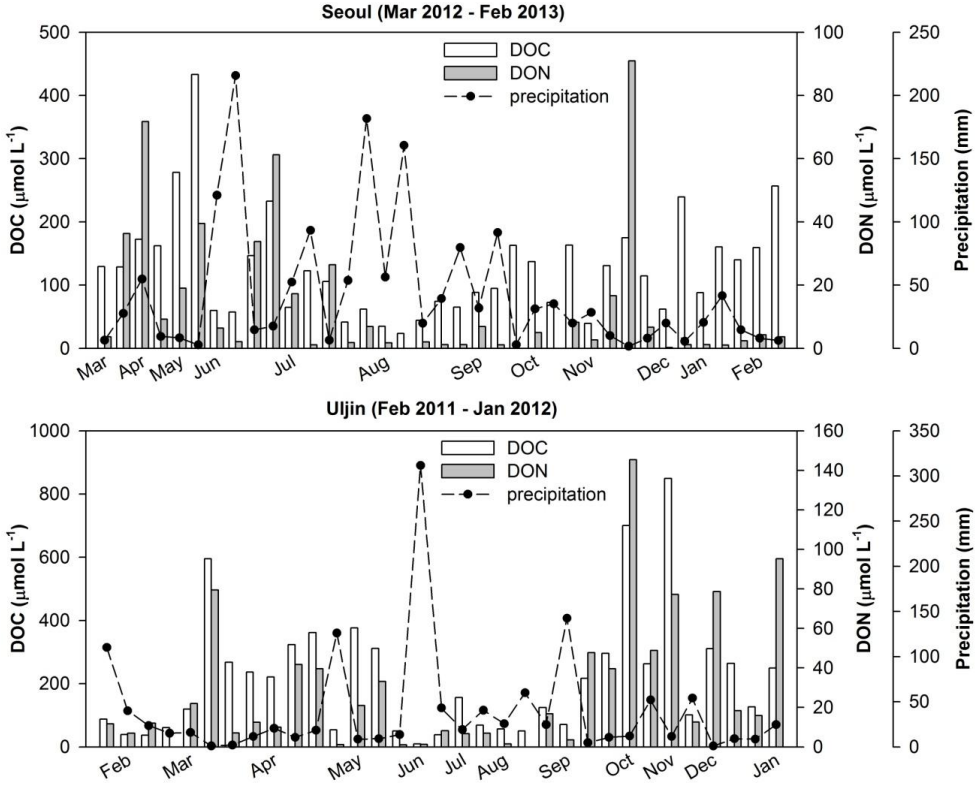


Figure 4.1. Concentrations of DOC and DON and precipitation amount for individual samples collected in Seoul (top) and Uljin (bottom).

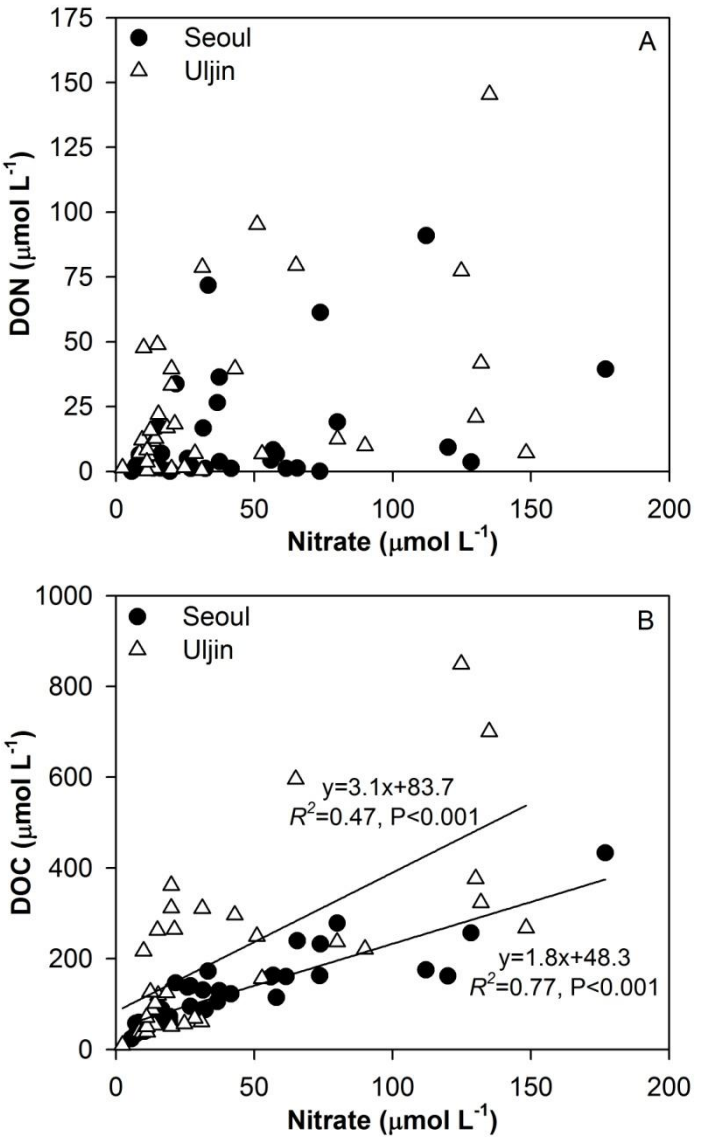


Figure 4.2. Correlations of nitrate with DON (A) and DOC (B) in precipitation of Seoul and Uljin.

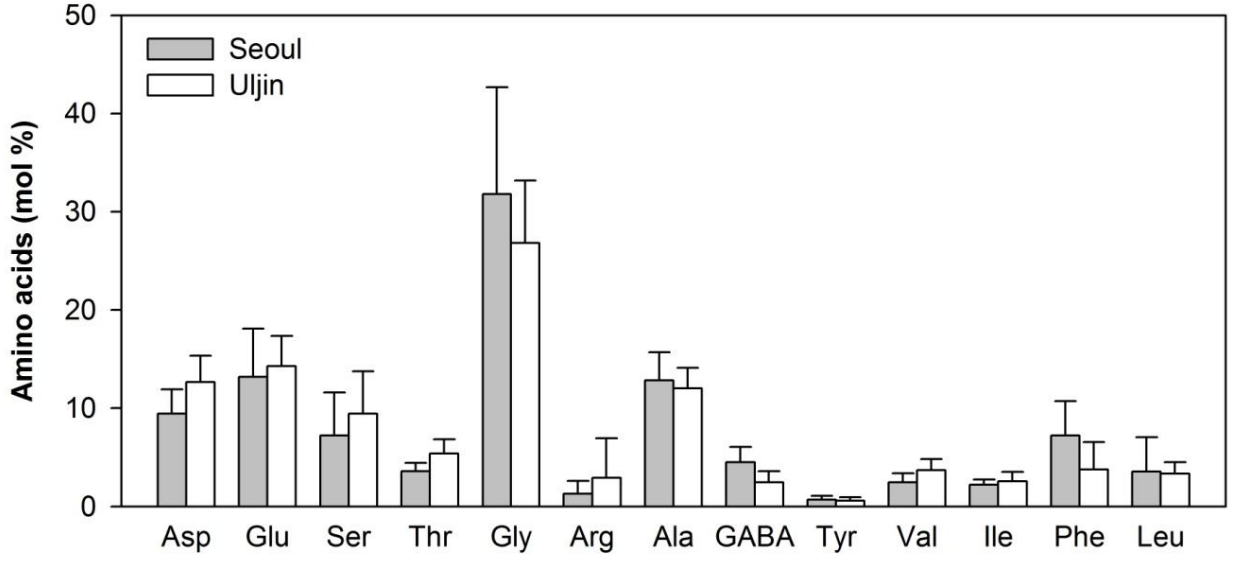


Figure 4.3. Average molar compositions of THAA in precipitation samples collected in Seoul and Uljin. Bars represent standard deviations. Abbreviations: Asp, aspartic acid; Glu, glutamic acid; Ser, serine; Thr, threonine; Gly, glycine; Arg, arginine; Ala, alanine; GABA, γ-amino butyric acid; Tyr, tyrosine; Val, valine; Ile, isoleucine; Phe, phenylalanine; Leu, leucine.

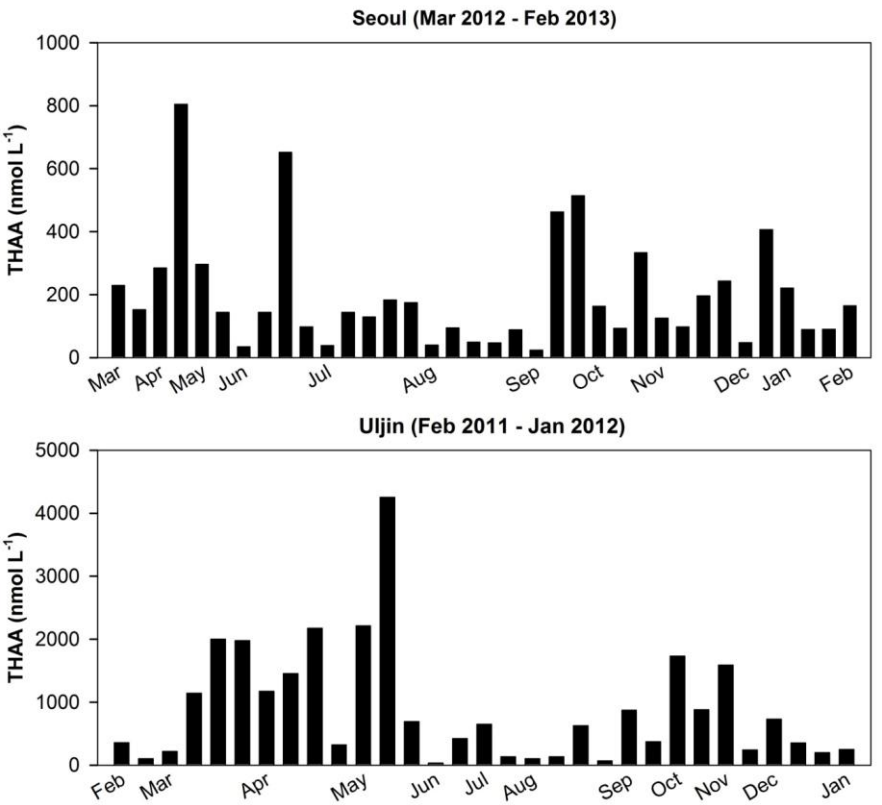


Figure 4.4. THAA concentrations in individual precipitation samples collected in Seoul (top) and Uljin (bottom).

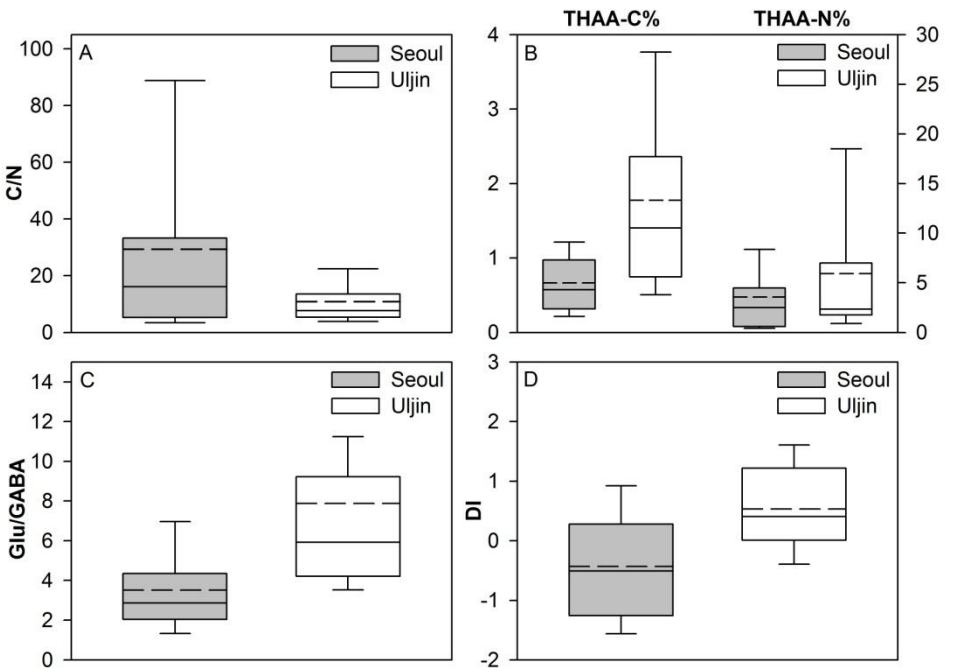


Figure 4.5. Box and whisker plots for qualitative indicators of DOM in precipitation of Seoul and Uljin: C/N (A), THAA-C% and THAA-N% (B), Glu/GABA (C), and DI (D). Boxes show the inter-quartile range of the data. Whiskers represent 90th and 10th percentiles. Solid and dash lines inside boxes indicate median and mean, respectively.

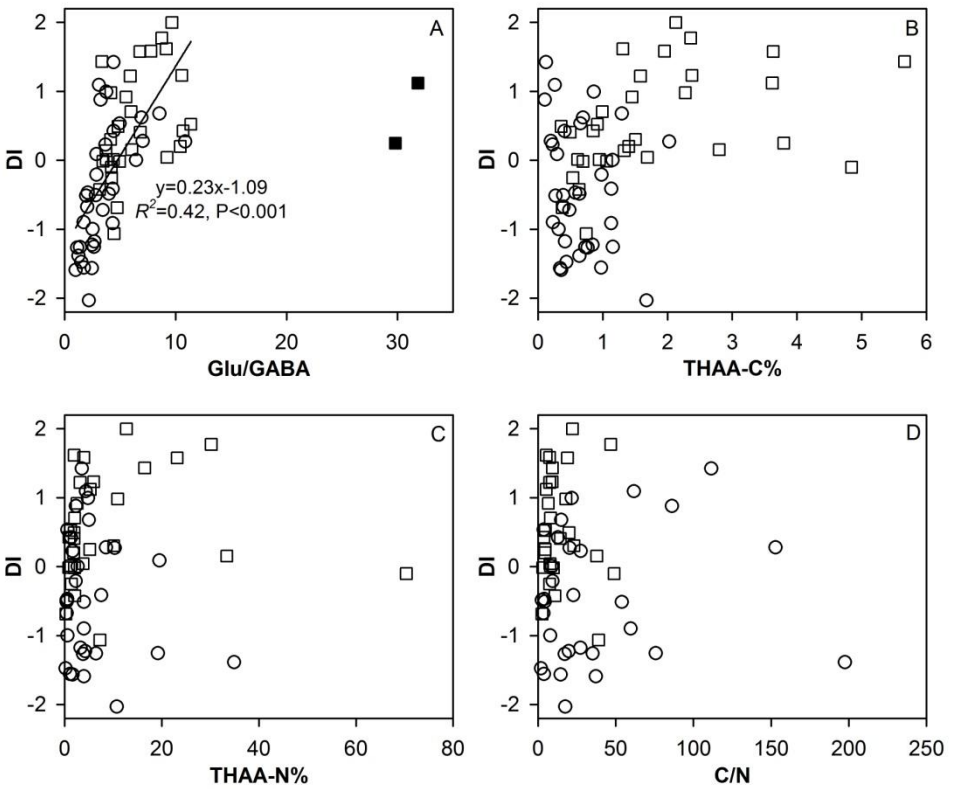


Figure 4.6. Plots showing correlations among qualitative indicators for all the samples collected in Seoul (empty circles) and Uljin (empty squares): DI versus Glu/GABA (A), DI versus THAA-C% (B), DI versus THAA-N% (C), and DI versus C/N (D). Filled symbols represent outliers.

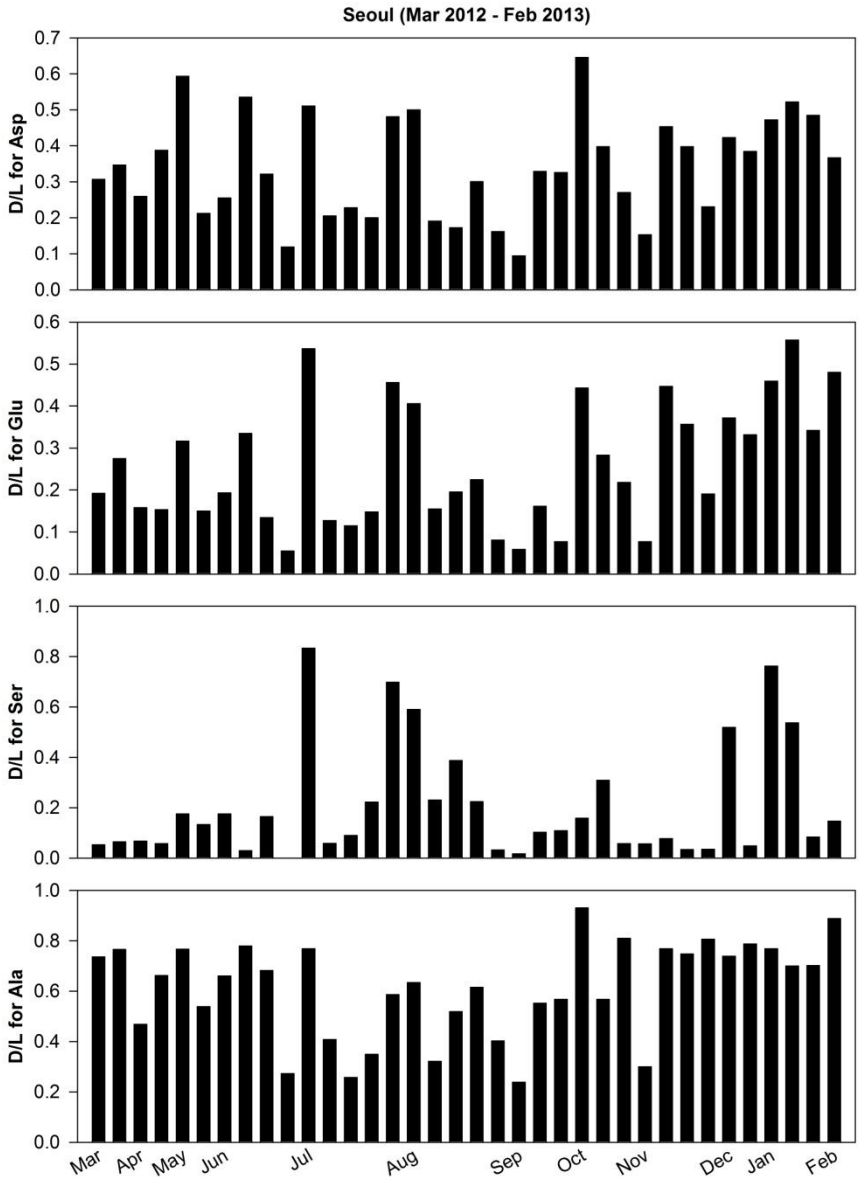


Figure 4.7. Temporal variations of D/L ratios for Asp, Glu, Ser, and Ala in precipitation samples collected at Seoul (2012–2013).

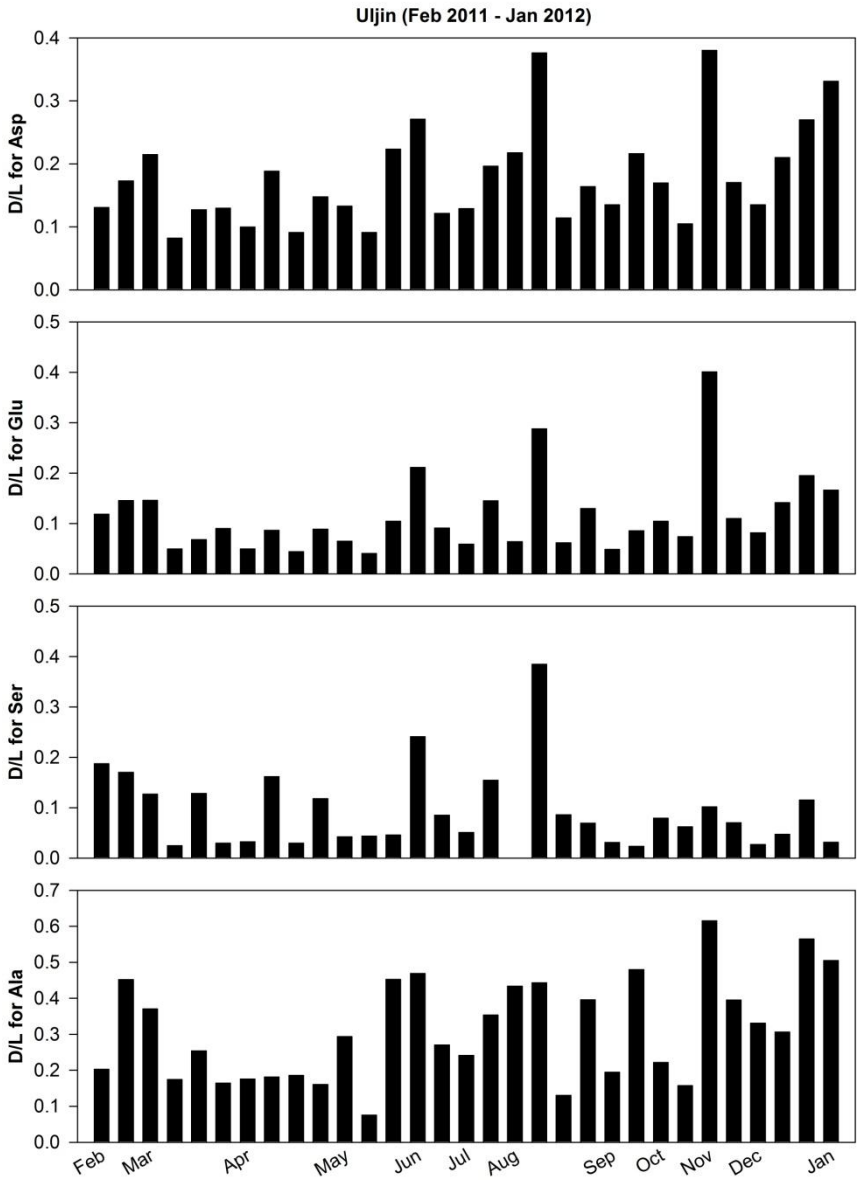


Figure 4.8. Temporal variations of D/L ratios for Asp, Glu, Ser, and Ala in precipitation samples collected at Uljin (2011–2012).

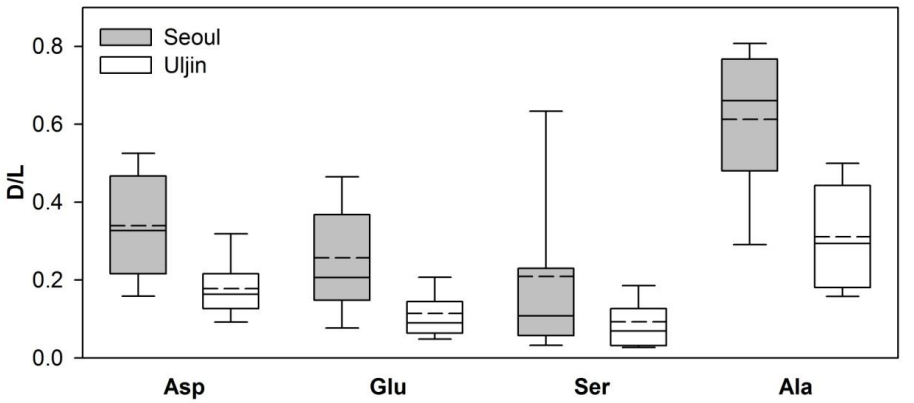


Figure 4.9. Enantiomeric ratios for specific amino acids in precipitation collected in Seoul and Uljin. Boxes show the inter-quartile range of the data. Whiskers represent 90th and 10th percentiles. Solid and dash lines inside boxes indicate median and mean, respectively.

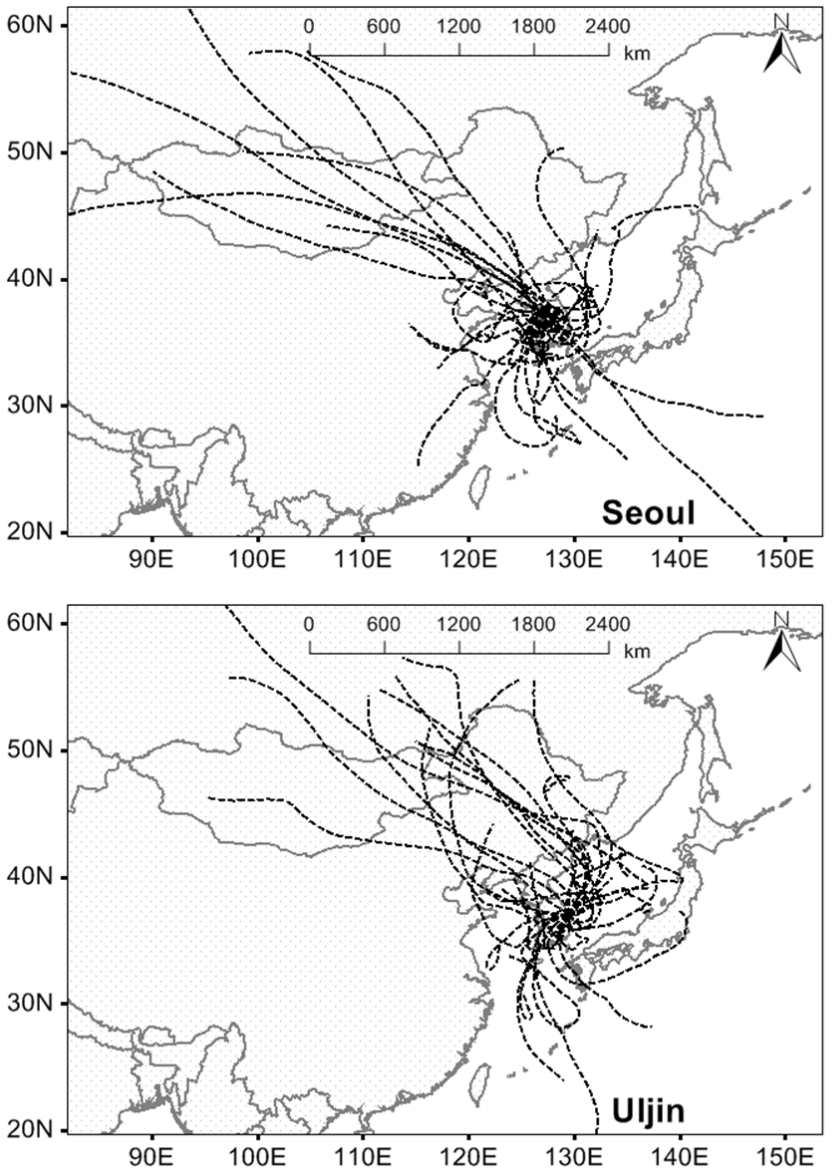


Figure 4.10. 72 h HYSPLIT air mass backward trajectories for precipitation events in Seoul (top) and Uljin (bottom). The proportions of air mass travel time over land or ocean can be roughly estimated using the trajectory lines.

Table 4.1. Descriptive statistics for DOC, DON, and THAA in precipitation samples collected in Seoul and Uljin.

	Min.	1st quartile	Median	3rd quartile	Max.	Mean	VWA[a]
Seoul (N=37)							
DOC (μmol L^{-1})	24	62	106	163	433	128	81
DON (μmol L^{-1})	BD[b]	2	4	17	91	15	8
THAA (nmol L^{-1})	23	90	144	230	804	197	117
Uljin (N=33)							
DOC (μmol L^{-1})	9	58	156	296	849	215	98
DON (μmol L^{-1})	BD	7	13	40	145	30	12
THAA (nmol L^{-1})	34	198	419	1450	4250	885	384

[a] Volume-weighted average.

[b] Below detection limit.

Table 4.2. Matrix of correlation coefficients of D/L ratios for precipitation samples collected at Seoul (2012–2013) and Uljin (2011–2012).

	Asp	Glu	Ser	Ala
Asp	1.00			
Glu	0.89	1.00		
Ser	0.51	0.65	1.00	
Ala	0.85	0.79	0.33	1.00

5. Sources and fluxes of organic nitrogen in precipitation over the southern East/Japan Sea: Potential impacts on marine productivity

5.1. Introduction

The availability of reactive nitrogen (or fixed nitrogen), including all nitrogen species except N_2, is often a determinant controlling the primary production in terrestrial and marine ecosystems (Vitousek and Howarth, 1991). However, since the mid-1800s the global nitrogen cycle has been significantly perturbed by excessive production of reactive nitrogen through human activities (at a similar rate to natural biological fixation) (Dentener et al., 2006; Galloway et al., 2008; Fowler et al., 2013), such as the Haber–Bosch process, fossil fuel combustion, and legume cultivation (Grubber and Galloway, 2008). A fraction of the reactive nitrogen is transported from continents to oceans via rivers, groundwater, and the atmosphere, exerting a significant influence on marine ecology and biogeochemistry (e.g., acidification, eutrophication, and oxygen depletion) (Seitzinger et al., 2005; Paytan et al., 2006; Doney et al., 2007; Krishnamurthy et al., 2010). In particular, the supply of external or "new" nitrogen to marine systems through atmospheric deposition can be substantial in some marginal and coastal seas (Beddig et al., 1997; Castro and Driscoll, 2002; de Leeuw et al., 2003; Uno et al., 2007, Zhang et al., 2010), as well as the open ocean (Galloway et al., 2004; Duce et al., 2008).

The East/Japan Sea (EJS) is a semi-closed marginal sea (covering an area of 1.01×10^6 km^2) surrounded by Russia, Korea, and Japan, which has been suggested to be an ideal site to investigate the impacts of atmospheric nutrient deposition on

the northwestern Pacific Ocean (Kim and Kim, 2013). It is a highly productive region where nitrogen is severely limited (Talley et al., 2004; Jenkins, 2008; Kim and Kim, 2013). Therefore, the supply of reactive nitrogen is particularly important in determining the primary productivity of this marine ecosystem. In addition to the upwelling of deep waters and N_2 fixation by diazotrophs within the ocean, land-derived reactive nitrogen (which is largely anthropogenic) can also contribute to the nitrogen required for primary production in the EJS. Since no major rivers flow into the EJS from the surrounding coasts, the fluvial inputs of nitrogen can be ignored (Kang et al., 2009; Yoo and Park, 2009). Nevertheless, terrigenous nitrogen transported via the atmosphere may reach the open ocean, contributing to the nitrogen inventory across the EJS. In fact, the mid- and long-range atmospheric transport of dust and pollutants from land to the northwestern Pacific Ocean (including the EJS) has been shown to be remarkable (Jo et al., 2007; Kang et al., 2009; Kang et al., 2011, Kim et al., 2011a; Zhang et al.,2011), particularly since this region is located downwind of East Asia, a densely populated area characterized by intensive emissions of aerosols and gases by anthropogenic and natural processes(Cooke et al., 1999; Richter et al., 2005; Kim, 2008). Recently, Kim et al. (2011a) suggested the significant atmospheric nitrogen deposition has switched extensive parts of the northwestern Pacific Ocean (including the EJS) from being nitrogen-limited to phosphorous-limited during the last three decades. A follow-up study by Kim et al. (2013), however, attributed this increasing trend in relative abundance of nitrogen over phosphorous to nutrient transport by ocean currents. Nevertheless, Kim and Kim (2013) argued that this oceanic region would remain nitrogen-limited for the next

100 years, based on observational data and model predictions. The debate aroused here signifies the importance of an unambiguous budget of nitrogen in the EJS, especially the fraction transported by the atmosphere, which is poorly constrained due to a lack of data (Zhang et al., 2011).

The atmospheric deposition of nitrogen over the southern EJS was previously evaluated by Kang et al. (2010) using dry deposition observations combined with estimates for wet deposition. However, their approximation on nitrogen deposition was an underestimate, since it did not take into account organic nitrogen, which is a globally significant constituent of total reactive nitrogen in the atmosphere (ca. 30% on average) (Jickells, 2006; Cape et al., 2011; Cornell, 2011). Indeed, the growing weight of evidence from global observational studies suggests that a considerable fraction of deposited nitrogen is in organic form (Cornell, 2011, and references therein), which is able to stimulate the productivity of bacteria and phytoplankton in the receiving marine ecosystems (Seitzinger and Sanders, 1999, Bronk et al., 2007). In particular, atmospheric organic nitrogen deposition was shown to be especially high over Asia (Cornell, 2011; Ito et al., 2014), implying it is imperative to incorporate this fraction into the budget of atmospheric nitrogen input to the EJS. Nevertheless, although quantitatively significant, the sources, chemical compositions, and bioavailability of atmospheric organic nitrogen are largely unknown (Mace et al., 2003a; Duce et al., 2008; Jickells et al., 2013), hindering our understanding of its biogeochemical role in the receiving ecosystems.

In order to provide better constraints on atmospheric nitrogen deposition to the EJS, I analyzed reactive nitrogen species (inorganic and organic) and major

ions in precipitation samples collected at a coastal site upwind of this marginal sea. The emphasis of the present work was placed on organic nitrogen, which has been ignored in previous study and is generally poorly characterized in comparison with its inorganic counterpart. With the aid of air mass back trajectory and factor analysis, the geographical and emission sources of organic nitrogen were explored. Moreover, using the calculated total nitrogen depositional flux, the fraction of new primary production of the EJS which is potentially supported by atmospheric nitrogen deposition was estimated.

5.2. Study site and sample collection

The sampling campaign was conducted at Uljin (37 °N, 129.4 °E), which is located on the eastern coastline of Korea (Fig. 5.1). It is a rural area with a small population of around 52,000 inhabiting an area of 989.06 km^2. Precipitation samples were collected on an event basis on the rooftop of a research facility at the Korean Institute of Ocean Science and Technology (East Sea branch) from February 2011 to January 2012. A home-made sampler was employed, which is composed of a polypropylene funnel (dia. 250 mm) connected by Tygon FEP-lined tubing to a high-density polyethylene (HDPE) bottle placed in a covered bucket. Prior to use, the apparatus was thoroughly cleaned using dilute hydrochloric acid and rinsed with deionized (Milli-Q) water (18.2 MΩ cm). The sampler was manually deployed at the onset of the precipitation events and retrieved after cessation. The impacts of dry deposition were minimized by restricting the exposure time to dry conditions (i.e., <1 h for daytime events or ≤5 h for overnight events). After collection, the samples were transferred to a laminar

flow clean room and filtered through pre-combusted (at 500°C) Whatman 0.7 μm GF/F glass fiber filters. Subsamples for dissolved organic carbon (DOC) analysis were placed in 20 mL pre-muffled glass ampoules (5 h at 500 ℃) and chemically preserved with 6 M pure hydrochloric acid, followed by fire sealing. Aliquots for dissolved nitrogen species and major ions were stored in pre-cleaned HDPE bottles and kept frozen at –20 ℃ until analysis.

5.3. Results and Discussion

5.3.1. Distributions of dissolved reactive nitrogen in precipitation

5.3.1.1. Concentrations and speciation

The concentrations of dissolved reactive nitrogen showed considerable variations during the sampling year, ranging from 2 to 428 μmol L^{-1} for NO_3^-, from 1 to 139 μmol L^{-1} for NH_4^+, and from below the detection limit to 145 μmol L^{-1} for DON, respectively (Table 5.1 and Fig. 5.2). Rather similar temporal trends were found for all three nitrogen species, with high abundances observed in spring and fall (Fig. 5.2). Aside from the source strength, the distribution pattern displayed here is likely to be influenced by several factors specific to this location. The precipitation amount might be one of the most important factors, because the variation patterns of these nitrogen species are in general accordance with the precipitation regime of Korea (particularly high in summer), in a manner that the concentrations decrease as the precipitation depth increases. In addition, the wind systems (or air mass origins) of Korea may also contribute significantly to the observed temporal trend (see section 5.3.1.2). The northwesterly prevails in most time of the year, transporting large amounts of terrestrially-derived nitrogen from

inland Korea and the Asian continent (especially China) to Uljin and the EJS. In contrast, the prevailing wind over the summer blows from the Pacific Ocean, carrying precipitation associated with relatively pristine air masses.

Overall, NO_3^- is the most abundant nitrogen species with an annual average concentration (AVG) of 58 μmol L^{-1} and a volume-weighted average (VWA) (Topol et al., 1985) of 20 μmol L^{-1}, followed by NH_4^+ (AVG = 39 μmol L^{-1}; VWA = 14 μmol L^{-1}) and DON (AVG = 30 μmol L^{-1}; VWA = 13 μmol L^{-1}) (Table 5.1). The reactive nitrogen concentrations in precipitation observed in this study are generally at the upper end of the range of literature values reported for coastal sites globally over the past decade (Keene et al., 2002; Luo et al., 2002; Mace et al., 2003b; Kieber et al., 2005; Calderon et al., 2007; Violaki et al., 2010; Cape et al., 2011; Zamora et al., 2011). However, much higher concentrations have been found in rainwater over coastal areas of China, which were attributed to significant pollutions associated with the rapid economic development (Chen et al., 2011; Zhang et al., 2012). The relatively high levels of reactive nitrogen in the atmosphere at Uljin probably can be linked to the anthropogenic emissions of nitrogen in East Asia including Korea and subsequent atmospheric transport.

In contrast to observations from regions characterized by intensive agricultural practices (e.g., China and midwestern USA) (Fahey et al., 1999; Zhang et al., 2008), NO_3^- showed higher abundances with respect to NH_4^+, implying that combustion processes contributed more significantly than agricultural activities to reactive inorganic nitrogen in the precipitation samples (Galloway et al., 2004; Spokes and Jickells, 2005; Lee et al., 2012). A few exceptions were observed in April, May, October, and November (Fig. 5.2), when

concentrations of NH_4^+ were similar to or higher than those of NO_3^-. These exceptions can be attributed to enhanced agricultural activities (i.e., application of N fertilizer and livestock manure to the farmland) during these time periods in Korea (Lee at al., 2012). Although being a minor component, DON made up a considerable fraction (28% on average) of the TDN in precipitation samples, approximating to that contributed by NH_4^+ (30% on average). In comparison with NO_3^- and NH_4^+, the relative proportion of DON showed remarkable variations from sample to sample, which were found to be relatively lower from April to August (Fig. 5.2). The seasonality and air mass origins might contribute to the pattern observed here to some extent. However, the major factors that control the proportion of organic nitrogen in atmospheric reactive nitrogen pool remain rather ambiguous (Cornell, 2011) (see section 5.3.3.1 for further discussion).

5.3.1.2. Potential source regions

Atmospheric deposition plays an important role in global biogeochemical cycles, as it allows chemical substances to be transported to locations remote from their source regions over relatively short time scales. Therefore, the reactive nitrogen found in the precipitation samples was presumably subject to influences of air masses originating from distant areas. In order to explore the potential source regions and to assess the contributions by long-range atmospheric transport, the provenances of the air masses corresponding to each of the precipitation events were determined based on air mass back trajectory (AMBT) analysis, using the GDAS dataset and the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (version 4) developed at the Air Resources

Laboratory of NOAA (Draxler and Hess, 1998). Apart from the nearby continental regions (i.e., the Korean Peninsula), reactive nitrogen could be transported over long distance to Uljin from mainland Asia as well as the surrounding oceans, as observed for other airborne species in Korea (Kim et al., 2005; Kim, 2008). Accordingly, based on calculated AMBTs, air mass origins were sorted into three groups: Korean Peninsula (Type I), Asian Continent (Type II), and Pacific Ocean (Type III) (Fig. 5.3). A similar classification regime can be found in Chapter 3, in which detailed descriptions for each group were presented. It is noteworthy that the reactive nitrogen in each group does not exclusively come from the corresponding source region identified. For example, the precipitation events associated with long-range transported air masses inevitably receive some contributions from local sources.

The distribution patterns of VWA concentrations for the three groups were consistent for NO_3^- and NH_4^+, with the highest concentrations observed in Type II and the lowest in Type III (Fig. 5.4). As these two nitrogen species are known to be predominantly anthropogenic, this pattern is consistent with the air-mass origins proposed for these groups. Type II air masses also account for the largest fraction (47%) of sampled precipitation events, suggesting a significant contribution to inorganic nitrogen at Uljin from the highly industrialized and urbanized areas of East Asia, especially eastern and northeastern China (Richter et al., 2005; Jeong and Park, 2008; Lee et al., 2014). The lowest VWA DON concentration was also observed for air masses derived from surrounding marine areas (Type III), implying that marine biogenic emission is an insignificant source for DON at Uljin. In contrast to the pattern seen for inorganic nitrogen, the

highest abundances of DON were associated with Type I air masses. It is thereby inferred that the emission sources within Korea play a dominant role in supplying organic nitrogen to the atmosphere at Uljin. Despite the fact that the largest concentrations of atmospheric organic nitrogen worldwide have been observed in China (Cornell, 2011), Type II air masses at Uljin were characterized by relatively lower DON abundances than Type I. This could be partially due to the inclusion of clean marine air masses and/or the loss of the labile portion of organic nitrogen during the long-range transport. In addition, the highest proportion of DON (32%) was also observed in Type I air masses, confirming the importance of organic nitrogen from emissions in Korea.

5.3.2. Source identification for DON

Whilst the major sources for inorganic reactive nitrogen in the atmosphere are known to be anthropogenic (Galloway et al., 2004; Fowler et al., 2013), the primary origins of the organic fraction remain poorly characterized (Cape et al., 2011; Cornell, 2011). Previous studies have suggested that atmospheric organic nitrogen may stem from a variety of natural and anthropogenic processes, including resuspension of soil dust, marine emissions, biomass burning, agricultural activities, industrial production, and fossil fuel combustion (Jickells et al., 2013 and references therein). In this study, attempts were made to identify the major sources of DON in the precipitation samples, on the basis of factor analysis in combination with major ions as tracers. The results obtained from varimax-rotated factor analysis suggest that most variations (91%) in the nine variables

included can be accounted for by three extracted factors (eigenvalue > 1) (Table 5.2).

The first factor is characterized by high loadings of Na^+, K^+, Mg^{2+}, Cl^-, and SO_4^{2-}. The enrichment factors (EFs) for these ions (except Na^+) with respect to average seawater composition were calculated using sodium as a reference element (Keene et al., 1986). The EFs fall in between 1 and 10 (Table 5.3), suggesting these chemical species are primarily derived from marine emissions (Poissant et al., 1994). This interpretation is confirmed by the significant positive correlations between the abundances of these ions and Na^+ (R^2 = 0.86 for K^+, 0.93 for Mg^{2+}, 0.98 for Cl^-, and 0.51 for SO_4^{2-}). Therefore, this factor probably can be attributed to the contributions from marine sources. The largest fraction of variance (50%) (Table 2) in the nine variables explained by this factor is consistent with the marine feature of Uljin. The second factor has high loadings of NO_3^- and Ca^{2+}, which are generally considered to be of different origins. In addition, moderate loadings are shown for NH_4^+ and SO_4^{2-} on this factor. In the atmosphere, NO_3^- is mainly derived from NO_2 emitted by fossil fuel combustion (Dentener et al., 2006), whereas Ca^{2+} comes from both crustal and marine sources (Gabriel et al., 2002). The relatively high EF value (19.17) indicates crustal contribution is more important for Ca^{2+} in the precipitation samples. This factor is therefore likely to represent a mixed source involving inputs from combustion processes as well as soil resuspension. The association of these ions (i.e., Ca^{2+}, NH_4^+, NO_3^-, and SO_4^{2-}) has frequently been observed in factor analysis conducted in previous studies (Hu et al., 2003; Wai et al., 2008; Song and Gao, 2009), and is attributed to the neutralization of acidic anions by alkaline cations in precipitation

(Wai et al., 2008). Since the loadings of DON on these two factors are rather low, the contributions from marine emissions, soil dust, and combustion-related processes to DON are expected to be less significant.

The third factor is associated with a moderate loading of NH_4^+ and a high loading of DON. NH_4^+ in precipitation is derived from its gaseous precursor NH_3, which is primarily released during agricultural activities such as animal husbandry and the application of synthetic fertilizer (Galloway et al., 2004). These activities are also known to be the origins of several important atmospheric organic nitrogen species (e.g., urea) (Cornell et al., 1998). According to statistical data from International Fertilizer Industry Association (2013), a considerable fraction of the nitrogen fertilizer consumed in Korea each year is in the form of urea. In addition, Lee et al. (2012) found NH_4^+ and DON in precipitation collected in a southern Korean city were mainly derived from fertilizer use and livestock excretion in surrounding rural areas using nitrogen isotopic analysis. This suggests that agricultural practices conducted within Korea could be a crucial source of NH_3 and organic nitrogen in the atmosphere, which is in line with the conclusions drawn from AMBT analysis that the Korean Peninsula contributes significantly to NH_4^+ and DON in the samples collected (Fig. 5.4). Taken together, it is concluded that the primary fraction of DON in the precipitation samples originated from agricultural activities in Korea, albeit contributions from other anthropogenic and biogenic sources cannot be ruled out.

5.3.3. Biogeochemical impacts of atmospheric nitrogen deposition on the EJS

5.3.3.1. Seasonal variations in nitrogen fluxes and DON proportions

The wet depositional fluxes (defined as the product of concentration and precipitation depth) of the three reactive nitrogen species showed remarkable seasonal variations, with relatively high values observed in spring and fall for NO_3^- and NH_4^+, and in fall and winter for DON, respectively (Fig. 5.5). While being a minor component in spring and summer, DON made up the largest fraction of the TDN fluxes in fall and winter. Precipitation amount is discounted as the cause of this temporal trend as it shows no correlation with the variations in nitrogen fluxes. The seasonal variations in nitrogen fluxes are mainly attributed to the strength of emission sources located in Korea as well as other distant regions (see the discussion in Section 5.3.1.2).

In addition, the relative distributions of DON, TDN, and DOC fluxes were found to be in good agreement over all seasons (Fig. 5.5), implying there might exist an inherent link among these species. A statistically significant positive correlation ($R^2 = 0.64$) was observed between the DON/TDN ratio and nitrogen to carbon atomic ratio (ON/OC) in dissolved organic matter in precipitation (Fig. 5.6). This study is the first to point out this correlation, but analysis of a larger dataset consisting of the available literature values and data obtained at Uljin and another location in Korea (Seoul) shows an even stronger correlation ($R^2 = 0.72$) (Fig. 5.6). The correlation found in this dataset is significant, since the data incorporate rainwater and aerosol samples collected worldwide from geographically varied locations (e.g., urban vs. rural, terrestrial vs. marine, and

anthropogenic vs. pristine) (Jordan et al., 1995; Eklund and McDowell, 1997; Campbell et al., 2000; Kieber et al., 2005; Miyazaki et al., 2010; Gioda et al., 2011). Therefore, the trend observed herein is likely not simply coincidental, but universal.

Variations in the ON/OC ratio of airborne organic matter could reflect source variations, as being suggested by previous studies (Neff et al., 2002; Cape et al., 2011; Kanakidou et al., 2012). Specifically, the highest ON/OC ratios were observed for aerosols over the remote North Pacific Ocean by Miyazaki et al. (2010), who also proposed that aerosols subject to increased biological influences were associated with higher ON/OC ratios. In contrast, the lowest ON/OC ratios were mostly found in precipitation samples collected in Seoul, where atmospheric organic matter is mainly derived from anthropogenic processes, especially fossil-fuel combustion (Yan and Kim, 2012). Atmospheric processing may also affect ON/OC ratios, as being seen in different types of aerosols that undergo various physical and photochemical atmospheric processes (Sun et al., 2011). In addition, it has been suggested that organic nitrogen tends to be less effectively removed from the atmosphere than inorganic nitrogen (Cornell, 2011 and references therein). Therefore, higher proportions of organic nitrogen might be linked to higher contributions from aged aerosols characterized by elevated ON/OC ratios (Sun et al., 2011).

The organic fraction of total reactive nitrogen in the atmosphere is highly variable in time and space, lacking a consistent trend on a global scale (Cornell, 2011; Jickells et al., 2013). In addition, the bioavailability of atmospheric organic nitrogen is poorly constrained (Duce et al., 2008; Kanakidou et al., 2012).

Therefore, despite the fact that organic nitrogen is increasingly recognized as a significant factor in the atmospheric deposition of reactive nitrogen, its biogeochemical impact on receiving ecosystems (especially the ocean) remains unclear. The empirical relationship found in the present study between ON/TN and ON/OC (Fig. 5.6) suggests that the utilization potential (evaluated using ON/OC ratios) of atmospheric deposited organic nitrogen by marine biota is positively correlated with its proportion in total atmospheric reactive nitrogen. Thus, atmospheric deposition of organic nitrogen may play a vital role in supplying bioavailable nitrogen to the surface layer of marine systems, especially when inorganic nitrogen is less abundant, as is the case for the northwestern Pacific Ocean.

5.3.3.2. Annual depositional fluxes of TDN at Uljin and over the EJS

The annual wet depositional flux is calculated to be 28 mmol N m^{-2} yr^{-1} for NO_3^-, 20 mmol N m^{-2} yr^{-1} for NH_4^+, and 19 mmol N m^{-2} yr^{-1} for DON, respectively (Table 5.4). My estimates of inorganic nitrogen fluxes are higher than those obtained for dry deposition by Kang et al. (2010) at Donghae (Fig. 5.1), a coastal site adjacent to the sampling location in this study. This is mainly due to the higher scavenging efficiency of airborne species by wet deposition comparing with dry deposition. In addition, the increasing anthropogenic emissions in East Asia may also contribute to this discrepancy (Galloway et al., 2004), as the sampling campaign by Kang et al. (2010) was conducted a decade ago. However, the fluxes of NO_3^- for both deposition modes were similar, which can be attributed to the effective dry scavenging of NO_3^- associated with coarse mode aerosols

(Nakamura et al., 2005; Matsumoto et al., 2009). In general, atmospheric depositional fluxes of reactive nitrogen are higher in the coastal areas of East Asia (including the western coast of the EJS) than at other coastal locations around the world (Table 5.4).This is in agreement with the distribution of oceanic regions characterized by the most intensive atmospheric nitrogen deposition on a global basis (Dentener et al., 2006; Krishnamurthy et al., 2007). The considerable contributions by DON to atmospheric TDN fluxes (7–50%) at these coastal/marine sites suggest the significant role of DON in supplying nitrogen to surface waters of the ocean.

Since the sampling site is located on the eastern coast of Korea, potential losses during transport must be considered when using the results of this study as a proxy for atmospheric depositional fluxes of reactive nitrogen over the remote EJS. Oki Island (Japan), an island located downwind of Uljin in the eastern section of the southern EJS (Fig. 5.1), is mainly influenced by air masses originating from China and Korea, and shows a similar wet depositional flux of inorganic nitrogen to the values found in this study (45 mmol N m^{-2} yr^{-1}, Japanese Acid Deposition Survey) (Kitayama et al., 2012). This implies that losses between the coast of Korea and offshore areas are small for wet depositional fluxes, as being shown for wet depositions of nitrogen over the eastern China Sea (Zhang et al., 2010). Therefore, my estimated atmospheric wet deposition flux can be extrapolated to the offshore region in the southern EJS. By taking the dry depositional flux of inorganic nitrogen observed at Oki Island (35 mmol N m^{-2} yr^{-1} for gases plus particles in 2003–2008) (Endo et al., 2011), the total (wet plus dry) inorganic nitrogen flux was calculated to be 83 mmol N m^{-2} yr^{-1}. Further, if

assuming the same DON/TDN ratio in dry deposition as in wet deposition, the total atmospheric depositional flux of reactive nitrogen (organic plus inorganic) amounts to 115 mmol N m^{-2} yr^{-1} over the southern EJS.

5.3.3.3. Biogeochemical implications

Considering the prevailing westerly winds and the anthropogenic origins of these atmospheric reactive nitrogen species, their atmospheric deposition represents a source of new rather than recycled oceanic nitrogen to the EJS. Therefore, the atmospheric deposition of this nitrogen could presumably fuel the new primary production of this marine ecosystem. While inorganic nitrogen is readily utilized by marine biota, organic nitrogen is only partially available. The bioavailability of atmospheric organic nitrogen is largely determined by its chemical composition. Specifically, most reduced organic nitrogen species (e.g., amino acids, urea, and amines) can be taken up by marine microorganisms on very short timescales, whereas the organic nitrogen associated with humic-like substances is probably refractory (Bronk et al., 2007). Incubation experiments estimate the bioavailability of atmospheric organic nitrogen to be 20–80% (Peierls and Paerl, 1997; Seitzinger and Sanders, 1999; Wedyan et al., 2007). Although not explicitly measured for the DON in the precipitation samples, a significant fraction is expected to be bioavailable, since it is mostly derived from agricultural activities that are known to produce large amounts of atmospheric reduced organic nitrogen, especially urea. Moreover, the severely N-limited conditions of the EJS are likely to promote the utilization of atmospheric organic nitrogen. Assuming a bioavailability of 20–80% for DON and 100% for inorganic nitrogen,

atmospheric deposition can supply approximately 89–109 mmol m^{-2} yr^{-1} of reactive nitrogen to support primary production in the southern EJS.

Using a Redfield C/N ratio of 6.625, this nitrogen flux can be converted to 7.1–8.7 g C m^{-2} yr^{-1} fixed by marine phytoplankton. This would account for 12–14% of new primary production in the southern EJS annually, which is taken to be 62 g C m^{-2} yr^{-1} based on the particulate organic carbon export fluxes reported by Hahm and Kim (2001) (using tritium and helium isotopes) and Kim et al. (2011) (using $^{234}Th/^{238}U$ disequilibrium). Our estimate is higher than those obtained by Onitsuka et al. (2009) using a coupled physical-ecosystem model (6–12% for the southern EJS from 1996 to 2003) and by Kang et al. (2010) based on field observations (ca. 10%) (Table 5.5). These discrepancies can be ascribed to the inclusion of organic nitrogen in this study as well as a potential increase of nitrogen deposition resulting from growing anthropogenic emissions over the past decade. On a global scale, the value obtained for the southern EJS is generally at the higher level, comparing with other oceanic regions (Table 5.5). Taking into account that the southern EJS (especially the Ulleung Basin) is highly productive (Hyun et al., 2009), the estimate obtained in this study is rather remarkable. Such high estimates can be explained by the exceptionally high levels of atmospheric anthropogenic nitrogen deposition over the coastal seas downwind of East Asia (Krishnamurthy et al., 2007; Duce et al., 2008). Moreover, the contribution of atmospheric reactive nitrogen to biological productivity in the southern EJS is expected to be more pronounced during summer to fall, when the upward flux of nitrogen from the deep layer is suppressed by water column stratification (Kang et al., 2010; Kim et al., 2011b).

The results presented here might be subject to large uncertainties, such as those associated with spatial variations of depositional fluxes across the EJS, the proportions of organic nitrogen in dry deposition, and the bioavailability of organic nitrogen in the atmosphere. Nevertheless, my estimation evidently suggests atmospheric transport represents a significant source of external nitrogen input to the southern EJS. Previous studies indicate that N_2 fixation is insignificant to the nitrogen budget of this marine system (Yanagi, 2002; Kang et al., 2010). Therefore, in addition to nitrogen upwelled from below the euphotic zone and transported by the Tsushima Warm Current through the Korea/Tsushima Strait (Onitsuka et al., 2007; Yoo and Park, 2009), atmospheric deposition could sustain a considerable fraction of the nitrogen demand by primary productivity in the southern EJS, especially the offshore region. Moreover, the elevated nitrogen deposition may modify the nutrient limitation regime (Duce et al., 2008) of the EJS and thus impact the phytoplankton community structure therein (Krishnamurthy et al., 2007; Galloway et al., 2008). Due to climate warming, El Niño is likely to become more prevalent in future, which could result in suppression of the nutricline and thus restriction of nutrient upwelling from deep waters (Mackey et al., 2010). Conversely, the anthropogenic nitrogen deposition over the northwestern Pacific Ocean is predicted to increase in the near future (Duce et al., 2008). Consequently, atmospheric deposition of nitrogen is expected to play an increasingly important role in the biogeochemistry of the northwestern Pacific Ocean and the EJS over the coming decades. Special attentions should be given to the organic fraction, since little is known with respect to its sources and

distributions, rendering the regulation of emission as well as the prediction on its future trend rather difficult.

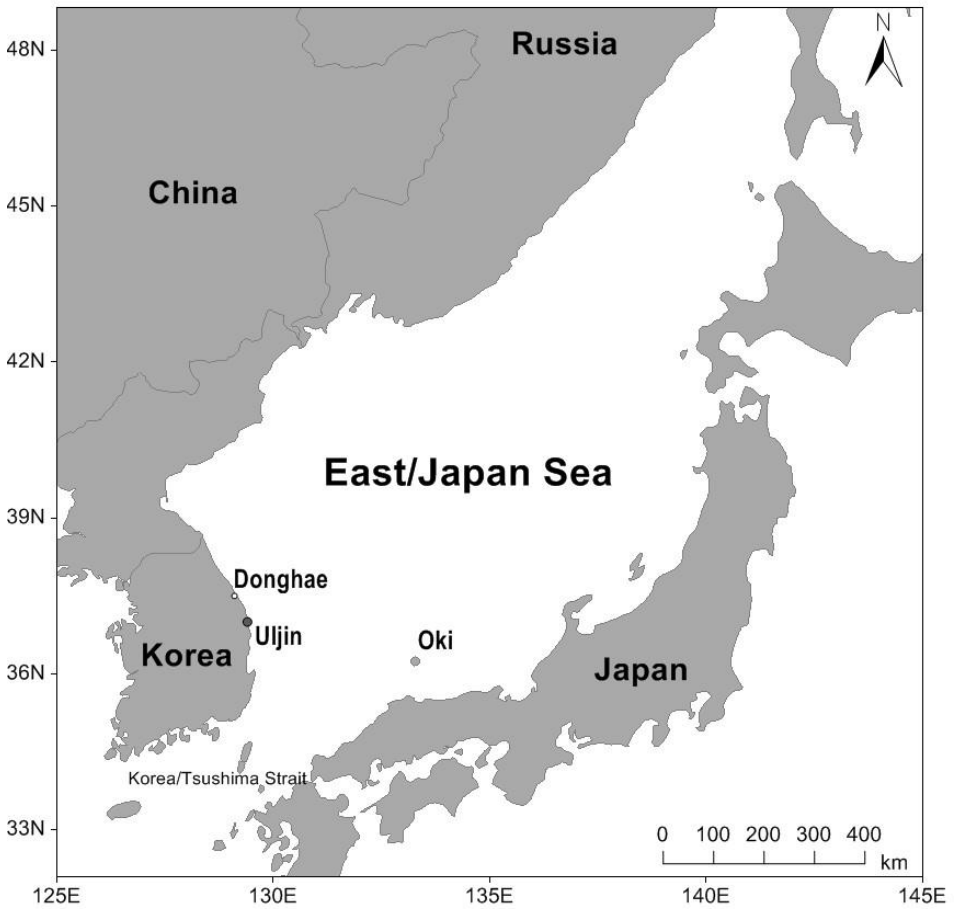


Figure 5.1. Map showing the location of Uljin (sampling site, 37 ℕ, 129.4 ℍ), Donghae (37.5 ℕ, 129.1 ℍ), and Oki Island (36.3 ℕ, 133.2 ℍ).

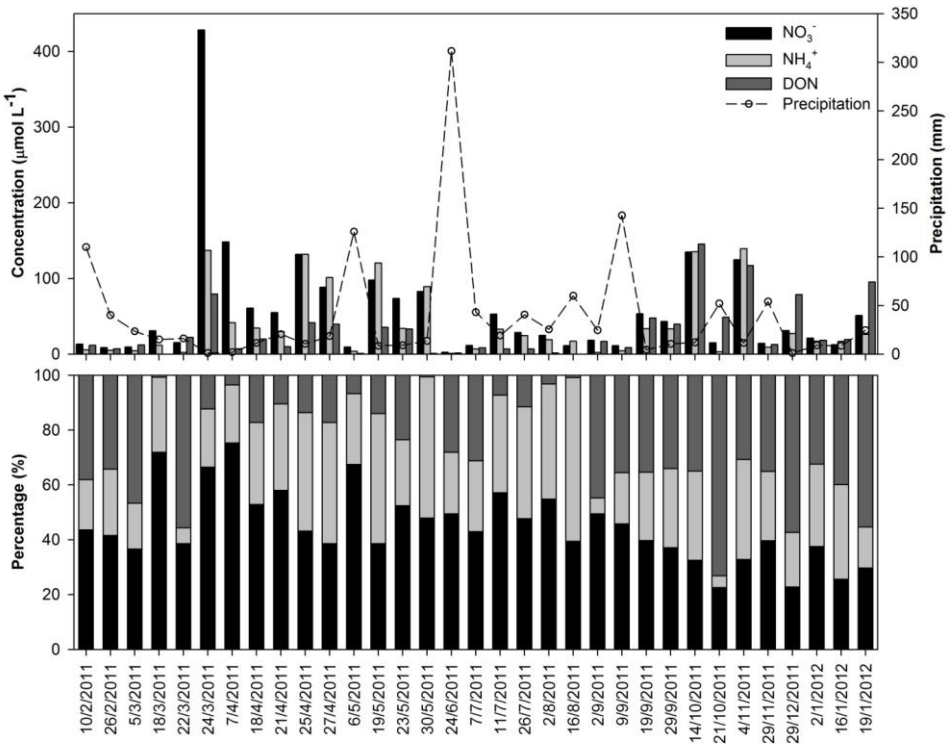


Figure 5.2. Concentrations (top) and percentages (bottom) of each reactive nitrogen species in precipitation samples collected at Uljin from 2011 to 2012.

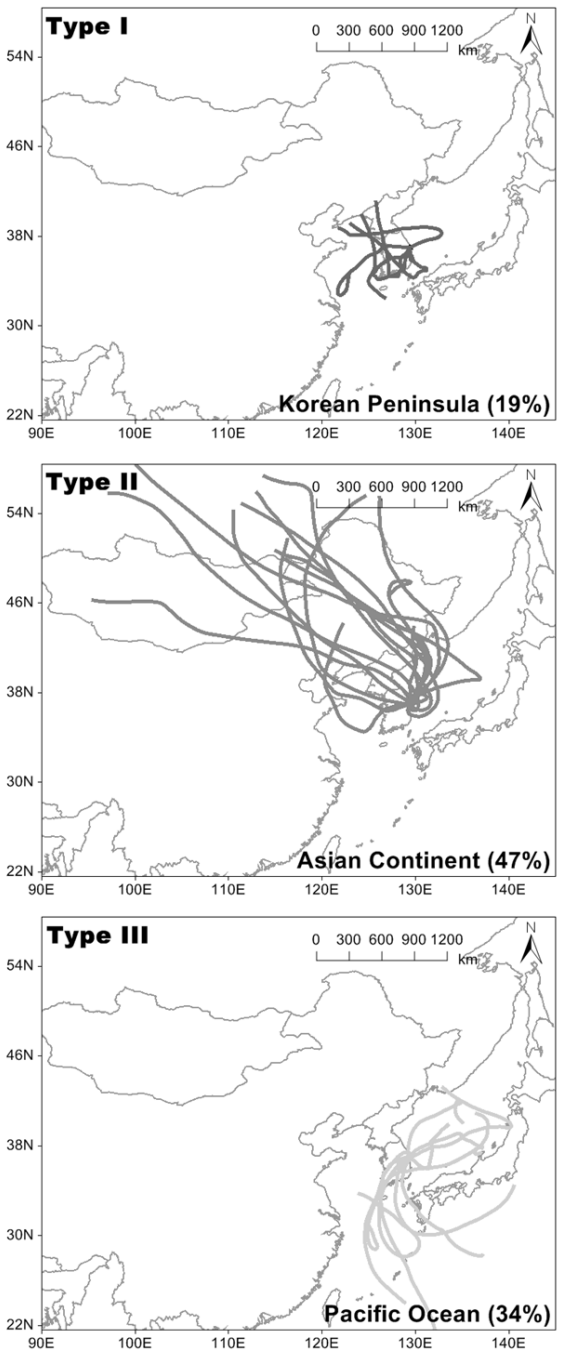


Figure 5.3. Three-day air mass backward trajectories at 500 m (above ground level) for precipitation events at Uljin during the sampling period, obtained using the HYSPLIT model. The air mass provenances are sorted into three groups: Korean Peninsula (Type I), Asian Continent (Type II), and Pacific Ocean (Type III). The percentage values in parentheses indicate the occurring frequencies of each type.

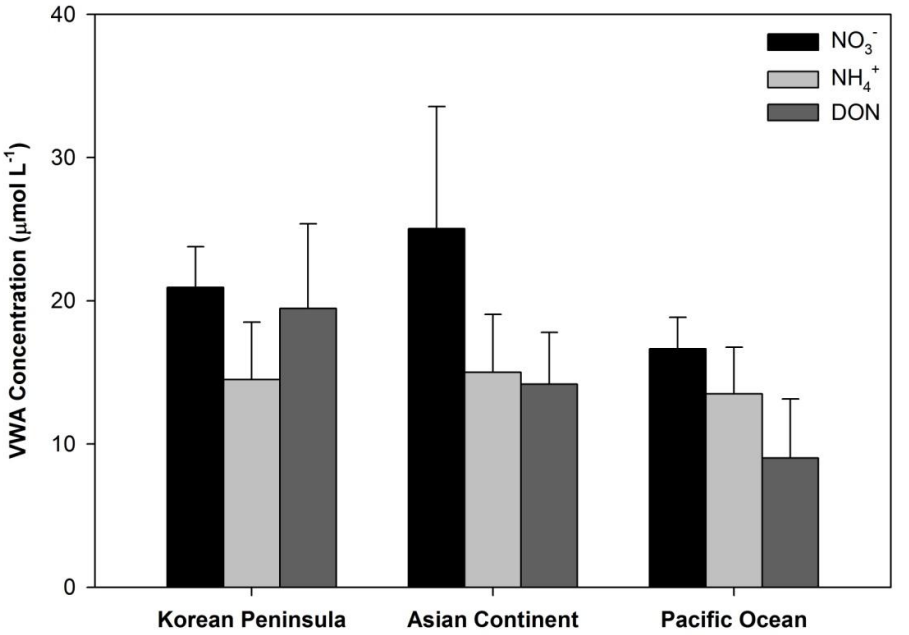


Figure 5.4. Volume-weighted average concentrations of reactive nitrogen species for precipitation events associated with the three types of air mass at Uljin. Error bars represent standard deviations.

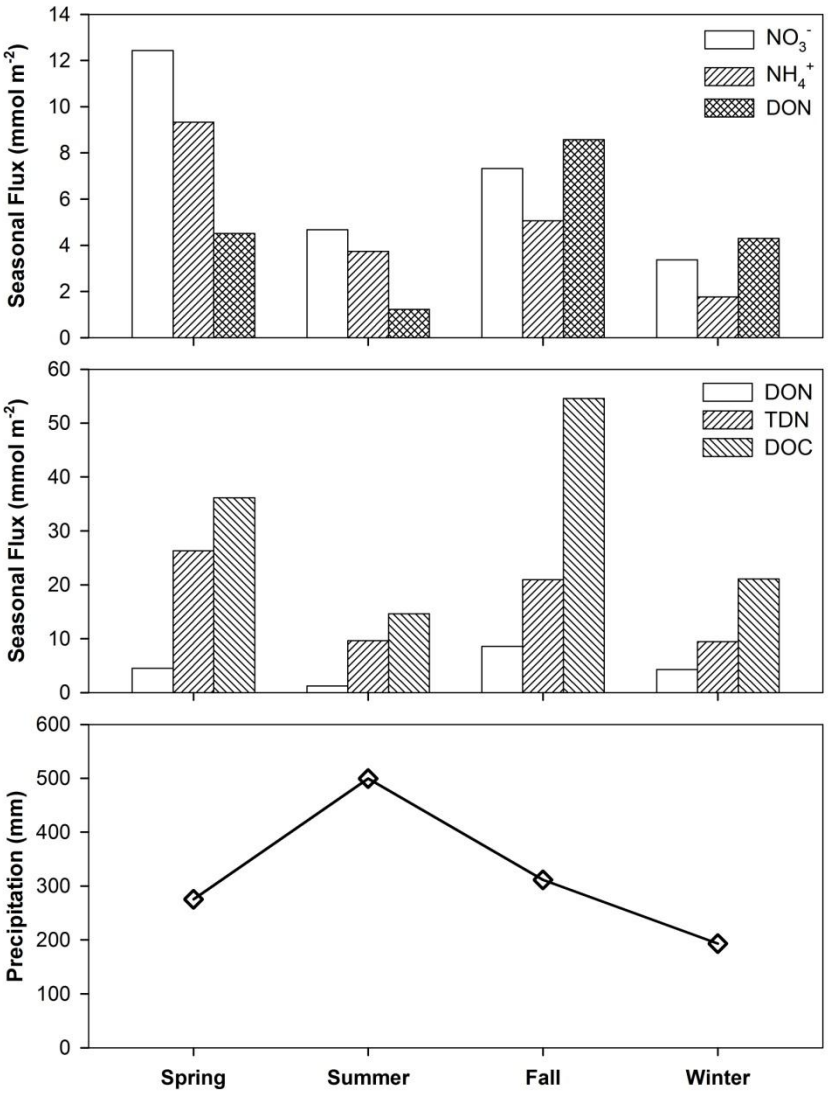


Figure 5.5. Seasonal wet depositional fluxes of NO_3^-, NH_4^+, DON, TDN, and DOC at Uljin. The precipitation amounts for each season are also shown.

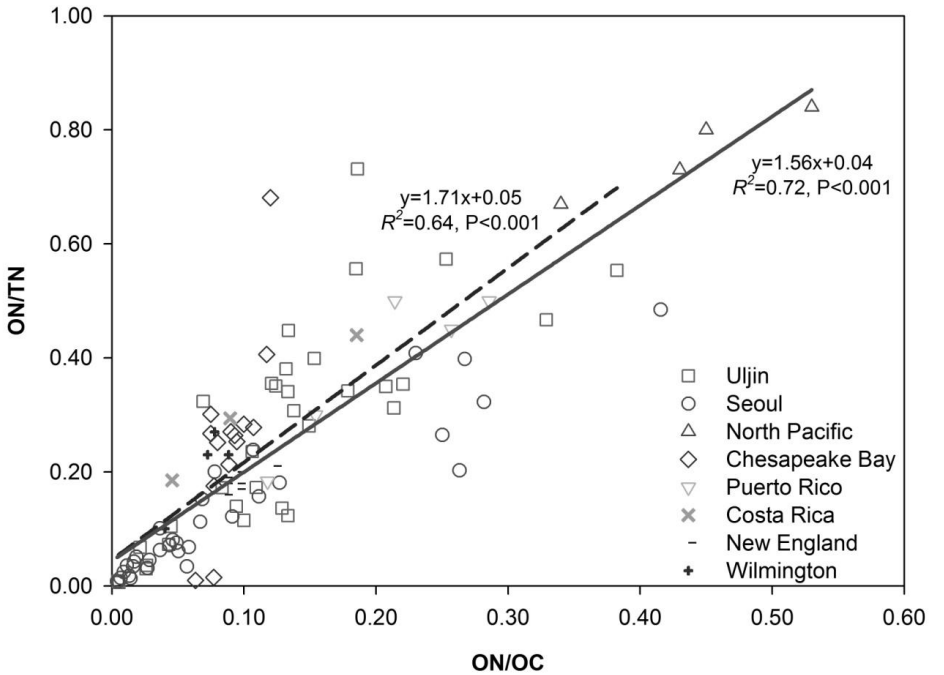


Figure 5.6. Plot of ON/TN versus ON/OC in precipitation samples collected at Uljin (N = 33) and Seoul (N = 33) in Korea and other locations worldwide, including the western North Pacific (aerosols, N = 4), Chesapeake Bay (N = 14), Puerto Rico (N = 5), Costa Rica (N = 3), New England (N = 15), and Wilmington (N = 4). The dashed line and solid line denote the best-fit correlations for Uljin data and the entire dataset, respectively.

Table 5.1. Statistical summary of concentrations of dissolved chemical species in precipitation analyzed in this study (unit: μmol L^{-1}).

	NO_3^-	NH_4^+	ON	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	SO_4^{2-}	OC
Min.	2	1	BD[a]	8	2	2	7	13	4	9
1st quartile	12	5	7	55	8	7	18	82	23	61
Median	31	24	13	138	15	28	46	206	58	156
3rd quartile	74	34	40	900	25	108	68	1580	117	296
Max.	428	139	145	2930	69	337	259	3780	215	849
Mean	58	39	30	635	21	76	57	894	83	219
VWA[b]	20	14	13	430	13	47	25	578	43	97

[a] Below detection limit.
[b] Volume-weighted average.

Table 5.2. Varimax-rotated principal factor matrix. [a]

	Factor 1	Factor 2	Factor 3
NO_3^-	-0.12	**0.94**	0.25
NH_4^+	-0.12	0.59	0.46
ON	0.20	0.27	**0.93**
Na^+	**0.98**	-0.05	0.10
K^+	**0.97**	0.12	0.10
Mg^{2+}	**0.99**	0.02	0.02
Ca^{2+}	0.22	**0.95**	0.09
Cl^-	**0.99**	-0.03	0.07
SO_4^{2-}	**0.75**	0.45	0.26
Eigenvalue	4.53	2.44	1.21
% Variance	50.35	27.09	13.47

[a] The software package used for principal factor analysis is SPSS 16.0.

Factor loadings exceeding 0.7 are shown in bold.

Table 5.3. Enrichment factors of major ions in precipitation at Uljin relative to seawater.

	K^+/ Na^+	Mg^{2+}/ Na^+	Ca^{2+}/ Na^+	Cl^-/ Na^+	SO_4^{2-}/ Na^+
Ratios in seawater	0.022	0.227	0.044	1.160	0.121
Ratios in precipitation	0.124	0.298	0.844	1.384	0.847
EF[a]	5.64	1.31	19.17	1.19	7.00

a The enrichment factor for a given ionic species X is calculated using the following equation: $EF = [X/Na^+]_{precipitation} / [X/Na^+]_{seawater}$.

Table 5.4. Annual atmospheric deposition fluxes of reactive nitrogen (mmol N m^{-2} yr^{-1}) at coastal and marine locations estimated based on long-term measurements during the last decade.

Location	Period	Deposition Mode	NO_3^-	NH_4^+	DIN	DON	%DON	Reference
Uljin, Korea	2011-2012	wet	28	20	48	19	28	This study
Donghae, Korea	2002-2003	dry	27	6	33	–	–	Kang et al. (2010)
Taiwan	2006	dry	–	–	39	22	36	Chen et al. (2010)
Shenzhen, China	1986-2006	wet	37	58	95	–	–	Huang et al. (2013)
Singapore	2007-2008	wet	51	26	77	34	31	He et al. (2011)
		dry	19	3	21	21	50	
Crete, Greece	2003-2006	wet	10	7	17	5	23	Violaki et al. (2010)
		dry	25	2	27	17	39	
Baltic Sea	2001-2002	wet pus dry	21	19	40	4	9	Rolff et al. (2008)
Tampa Bay, USA	2005	wet	23	10	33	2	6	Calderon et al. (2007)
Barnegat Bay, USA	1999-2001	wet	29	19	48	–	–	Gao (2002)
		dry	4	2	6	–	–	
Miami, USA	2007-2009	wet	15	12	27	2	7	Zamora et al. (2011)
Puerto Rico	2004-2007	wet	6	4	10	7	41	Gioda et al. (2011)

Table 5.5. Fractions of new primary production supported by atmospheric nitrogen input in world oceans on an annual basis.

Ocean Regions	Deposition Mode	Nitrogen Species	Contribution to New Production	Method	Reference
Southern East/Japan Sea	wet plus dry	TDN	12–14%	field observation	This study
Southern East/Japan Sea	wet plus dry	DIN	~10%	field observation	Kang et al. (2010)
East/Japan Sea	wet plus dry	DIN	2–12%	modeling	Onitsuka et al. (2009)
Southern Yellow Sea	wet plus dry	DIN	10.5%	field observation	Lv et al. (2005)
Yellow Sea	wet plus dry	TDN	0.3–6.7%	field observation	Qi et al. (2013)
Southern East China Sea	dry	TDN	8.3%	field observation	Chen et al. (2010)
East China Sea	wet plus dry	DIN	1.1–3.9%	modeling	Zhang et al. (2010)
East China Sea	dry	DIN	0.1–9%	field observation	Nakamura et al. (2005)
South China Sea	wet plus dry	TDN	20%	modeling	Kim et al. (2014a)
Bay of Bengal	dry	TDN	up to 25%	field observation	Srinivas and Sarin (2013)
Arabian Sea	dry	TDN	<1%	field observation	Srinivas and Sarin (2013)
Southeast Mediterranean Sea	wet plus dry	DIN	8–20%	field observation	Herut et al. (1999)
Western Mediterranean Sea	wet	DIN	10–20%	field observation	Loye-Pilot et al. (1993)
Eastern Atlantic	wet plus dry	DIN	4–6%	field observation	Neuer et al. (2004)
Bermuda	wet	TDN	7–15%	field observation	Kim et al. (2014b)
World Oceans	wet plus dry	TDN	1.5–6.9%	modeling	Duce et al. (2008)
World Oceans	wet plus dry	DIN	5.1%	modeling	Krishnamurthy et al. (2010)

6. Summary and conclusions

This dissertation documents a field-observation based study that investigates sources, fluxes, speciation, and biogeochemical characteristics of dissolved organic matter in precipitation collected at two sites with contrasting environmental settings in Korea. The results presented in this study contribute to the integrity of knowledge regarding atmospheric organic matter from the biogeochemical perspective, improving our understanding of the global biogeochemical cycles, especially with respect to carbon and nitrogen.

In Chapter 3, the annual volume-weighted average concentration of DOC in precipitation over Seoul was determined to be 94 μM, which falls in between averages for continental and coastal areas on a global scale. It is further found that its concentration levels were influenced by storm origin and precipitation amount, yet independent of seasonality or the length of dry period prior to precipitation. In addition, the DOC was shown to be derived predominantly from local emissions by the combustion of fossil-fuels, although the contribution by long-range transport from China can be substantial. Moreover, the annual wet depositional flux of DOC in Seoul was calculated to be 1.9 g C m^{-2} yr^{-1}. The global magnitude of fossil-fuel derived organic carbon dissolved in precipitation was further quantified to be 36 ±10 Tg C yr^{-1}. This empirical estimate could contribute to the constraint of magnitude of atmospheric organic carbon as well as the quantitative evaluation of the impacts of fossil-fuel combustion on the Earth's environment and human health.

In Chapter 4, DON in precipitation at both Seoul and Uljin were found to be derived mainly from natural/biological sources, whereas DOC was mostly (Seoul)

or partially (Uljin) from anthropogenic sources. The different bulk compositions of DOM at these two sites (reflected by qualitative indicators) were mainly attributed to differences in contributing sources rather than different diagenetic states. Moreover, the diagenetic history of amino acids was shown to be decoupled from that of bulk atmospheric OM. Furthermore, much higher enantiomeric (D/L) ratios of amino acids were observed at Seoul than at Uljin, which might result from more advanced diagenetic stages as well as higher contributions from bacteria inhabiting terrestrial environments. In addition, the C- and N-normalized yields of D-alanine in DOM of precipitation samples were found to be comparable to literature values reported for aquatic systems, where a significant portion of DOM was suggested to be of bacterial origin. The results presented in this Chapter suggest that bacteria and their remnants might constitute an important fraction of OM in the atmosphere. However, more intensive future studies are necessary to provide a quantitative constraint on the bacterial contribution to atmospheric OM.

In Chapter 5, inorganic nitrogen in precipitation collected at Uljin was found to be mostly derived from the Asian Continent (particularly eastern and northeastern China) through long-range atmospheric transport, whereas the primary sources of DON are distributed within Korea. Furthermore, agricultural activities (e.g., animal husbandry and the application of synthetic fertilizer) were identified as the major emission source for DON. A positive correlation was found between the proportion of organic nitrogen in total reactive nitrogen and nitrogen to carbon ratio in organic matter, implying that the biogeochemical impact of organic nitrogen deposition is especially significant (i.e., more

bioavailable) when inorganic nitrogen is less abundant. By combining the wet depositional flux recorded at Uljin with the dry depositional flux reported for Oki Island, the total (wet plus dry) atmospheric deposition of reactive inorganic and organic nitrogen to the southern EJS was estimated to be 115 mmol N m^{-2} yr^{-1}. This flux could potentially support 12–14% of the new primary production of the southern EJS on an annual basis, of which up to 3.4% would be attributed to organic nitrogen. The results presented in this Chapter emphasize the significant impact of atmospheric nitrogen deposition on the biogeochemistry of the EJS and by extension the northwestern Pacific Ocean. The development of this impact in response to climate change and growing anthropogenic emissions should be routinely monitored, especially in the case of organic nitrogen. More extensive information might be required to better understand the biogeochemical role of atmospheric nitrogen deposition, such as microorganisms community structure, the availability of other limiting nutrients (e.g., Fe and P), and the quantity and bioavailability of the insoluble fraction of organic nitrogen.

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요약(국문초록)

유기물질은 대기 중 어디에나 존재하는 주요 화학성분으로, 기후변화에서부터 사람의 건강에 이르기까지 다양한 분야에서 중요한 역할을 한다. 또한, 유기물질은 전 지구적 생지화학 순환과 영양염에 중요한 부분을 차지하는 것으로 인식되어 왔지만, 그에 대한 연구는 미미하다. 생지화학적 순환에서 대기 중 유기물질의 역할을 이해하기 위해, 한반도 내 두 연구지역(서울과 울진)을 선정하여 장기 관측(2009-2013)를 통해 강수 중 용존유기물질의 기원, 플럭스, 생지화학적 특성에 대하여 조사하였다.

서울에서 용존유기탄소(DOC)의 농도는 15 μM 에서 780 μM 의 범위를 보였고, 가중평균농도값은 94 μM 였다. 일반적으로 인정되는 추적자를 사용한 결과, 화석연료의 연소가 주요한 기원으로 밝혀졌다. Air mass backward trajectory analyses 를 이용하여, 강수 중 용존유기탄소는 한반도 내부 지역에서 대부분 발생하였고, 동중국과 북동중국으로부터의 장거리 수송도 상당히 영향을 주는 것으로 판단된다. 서울과 세계 다른 도심지역에서 강수 중 고정 유기탄소(relatively invariant organic carbon)와 황(sulfur)간의 질량 비율을 고려해보면, 전 지구적으로 화석연료를 통한 습성 침적(wet depositional) 용존유기탄소의 양은 36±10 Tg C yr^{-1}로 계산되었다.

Air mass backward trajectory analyses 으로 울진에서 채수한 강수시료 중 무기질소(NO_3^-와 NH_4^+)의 기원을 분석한 결과, 상당 부분이

아시아대륙으로부터 유입된 것으로 판단되고, 용존유기질소(DON)는 한반도 내에서 기원한 것으로 판단된다. 추적자로써의 주요 이온들과 조합하여 직교회전(varimax-rotated) 요인분석을 한 결과 한반도 내 농업활동이 용존유기질소의 주요 기원으로 나타났다. 또한, 울진 강수 시료에서 총 반응성(reactive) 질소 중 유기성분의 크기와 유기물 중 질소 대 탄소의 원소 비율 사이에 양의 상관관계를 보였다. 이 상관관계는 세계 다른 지역에서도 관측되는데, 대기 중 유기질소의 사용가능성은 총 질소 중 유기질소의 비율에 따라 증가함을 의미한다. 이 연구에서 측정된 습성 침적양과 이전 연구에서 측정된 동해 외딴섬에서 측정된 건성(dry deposition) 침적양을 이용하여, 대기를 통해 동해 남부로 유입되는 반응성 질소의 총 플럭스는 115 mmol N m^{-2} yr^{-1}로 계산되었다. 이러한 결과는 대기를 통한 질소, 특히 유기물 성분의 공급에 의해서 북서 태평양의 일차생산(primary production)에 상당한 기여를 할 것으로 보인다.

서울(도심지역)에서 평균 용존유기탄소, 용존유기질소, 총 가수분해성(total hydrolyzable) 아미노산의 평균농도는 울진(연안 농촌지역)에 비해 낮은 값을 보였다. 두 지역에서 용존유기물질의 서로 다른 벌크조성(bulk composition)은 주로 기여하는 기원의 차이에 따른 것이다. 4 가지 아미노산(aspartic acid, glutamic acid, serine, alanine)의 D-enantiomers 은 강수시료에 모두 존재하였다. 울진보다 서울에서 보다 높은 D/L 아미노산 비율이 나타나는 것은 육상환경에 서식하는 박테리아의 영향과 보다 더 진행된 속성작용(advanced

diagenetic stages)으로 나타난 것으로 판단된다. 강수 시료에서 D-alanine 의 탄소와 질소로 정상화된 수득률(normalized yield)은, 용존유기물질의 대부분이 박테리아기원으로 알려져 있는 해양환경에서 보고된 값과 유사하게 나타났다. 이 결과는 박테리아와 박테리아의 잔류물(remnants)이 대기 유기물의 중요한 부분을 구성하고 있음을 나타내며, 대기 중 유기물의 질과 표층 생태계에 침적 된 이후 생물학적 이용 가능성(bioavailability)에 상당한 영향을 주는 것으로 판단된다.

이 연구는 생지화학적 관점에서 대기 중 유기물질에 대한 우리의 이해에 기여한다. 이는 대기 중 유기물의 화학적 분화(chemical speciation)와 생물학적 이용가능성과 같은 생지화학적 역할에 관한 종합적인 지식을 위한 포괄적인 추가 연구가 필요함을 강조한다.

주요어: 유기물질, 생지화학적 순환, 대기, 습성 침적, 유기탄소, 유기질소

학번: 2008-22477

Appendix: Supplemental Information for Chapter 4

Table S1. Precipitation depth, DOC, DON, NO_3^-, and THAA concentrations, qualitative indicator values, and air mass travel time over the ocean for precipitation events sampled at Seoul (2012–2013) and Uljin (2011–2012).

Date[a]	Precipitation (mm)	DOC (μmol L^{-1})	DON (μmol L^{-1})	NO_3^- (μmol L^{-1})	THAA (nmol L^{-1})	Qualitative indicators					Air mass over ocean (%)[b]
						C/N	Glu/GABA	DI	THAA-N%	THAA-C%	
Seoul											
16/3/2012	6	130	3.7	37	229	35	1.4	-1.3	6.5	0.7	67
23/3/2012	28	129	36	37	152	3.5	2.0	-0.7	0.4	0.4	0
2/4/2012	55	173	72	33	284	2.4	4.0	-0.5	0.4	0.6	33
10/4/2012	9	162	*9.2*[c]	120	804	*18*	2.2	-2.0	*10.7*	1.7	83
14/5/2012	8	278	19	80	296	15	2.4	-1.6	1.6	0.3	83
17/5/2012	3	433	40	177	—	11	—	—	—	—	67
29/6/2012	121	60	6.4	8.4	144	9.3	2.9	-0.2	2.3	1.0	33
5/7/2012	216	58	2.1	7.2	34	28	3.7	0.2	1.6	0.2	42
10/7/2012	15	147	34	22	144	4.3	2.8	-0.5	0.4	0.4	42
13/7/2012	18	233	61	74	651	3.8	1.7	-1.6	1.1	1.0	58
14/7/2012	52	65	17	15	98	3.7	5.0	0.5	0.6	0.7	42
18/7/2012	93	123	1.1	42	38	112	4.4	1.4	3.5	0.1	75
22/7/2012	6	106	27	37	144	4.0	2.1	-0.5	0.6	0.6	17
12/8/2012	54	42	1.8	11	129	23	4.3	-0.4	7.5	1.1	58
14/8/2012	182	62	6.9	16	183	9.0	6.4	0.0	2.7	1.2	67
18/8/2012	56	35	1.7	7.4	174	20	11	0.3	10.3	2.0	50
20/8/2012	161	24	BD[d]	5.6	40	—	6.9	0.6	—	0.7	88
24/8/2012	20	44	2.0	11	94	22	3.7	1.0	4.8	0.9	75
30/8/2012	39	74	1.2	16	49	62	3.1	1.1	4.4	0.3	67
4/9/2012	80	65	1.2	13	46	54	1.9	-0.5	3.9	0.3	75

Table S1. Continued.

7/9/2012	32	89	6.9	17	88	13	4.4	0.4	1.3	0.4	17
16/9/2012	92	95	1.1	27	23	86	3.2	0.9	2.3	0.1	92
17/10/2012	3	163	BD	74	514	—	4.3	-0.9	—	1.1	33
22/10/2012	31	137	5.0	26	163	27	2.7	-1.2	3.3	0.4	79
27/10/2012	35	72	BD	20	93	—	3.4	-0.7	—	0.5	25
4/11/2012	20	163	8.2	57	333	20	2.5	-1.2	4.2	0.8	50
11/11/2012	29	40	2.6	10	125	15	8.6	0.7	5.0	1.3	58
16/11/2012	10	131	17	32	97	7.9	2.5	-1.0	0.6	0.3	33
25/11/2012	2	175	91	112	196	1.9	1.5	-1.5	0.2	0.4	58
5/12/2012	8	114	6.7	58	243	17	1.1	-1.3	3.8	0.8	25
14/12/2012	20	62	BD	19	47	—	2.9	0.1	—	0.3	33
29/12/2012	6	240	*1.2*	66	406	*198*	1.2	-1.4	*34.9*	0.6	33
21/1/2013	21	88	*1.2*	32	221	*76*	2.6	-1.3	*19.2*	1.2	0
1/2/2013	422	161	1.1	62	89	153	7.0	0.3	8.5	0.2	67
3/2/2013	15	140	2.3	27	89	60	1.7	-0.9	3.9	0.2	92
5/2/2013	8	159	*4.3*	56	165	*37*	1.0	-1.6	*4.0*	0.4	33
28/2/2013	6	257	*3.6*	128	—	*71*	—	—	—	—	67
Uljin											
10/2/2011	110	88	12	13	356	7.6	5.9	1.2	3.2	1.6	33
26/2/2011	40	39	7.0	8.5	—	5.6	—	—	—	—	33
5/3/2011	24	37	12	9.4	101	3.0	3.5	0.0	0.9	1.1	67
18/3/2011	15	61	BD	31	219	—	3.7	0.1	—	1.3	42
22/3/2011	16	119	22	15	1140	5.4	32	1.1	5.3	3.6	33
24/3/2011	1	595	79	65	—	7.5	—	—	—	—	0
7/4/2011	2	268	*7.1*	148	2000	*38*	6.1	0.2	*33.4*	2.8	20
18/4/2011	12	237	13	80	1970	19	6.8	1.6	23.2	3.6	42
21/4/2011	21	221	10	90	1170	22	9.7	2.0	12.7	2.1	58

Table S1. Continued.

25/4/2011	11	323	42	132	1450	7.8	9.2	0.0	3.8	1.7	25
27/4/2011	19	362	40	20	2170	9.1	11	1.2	6.0	2.4	58
6/5/2011	126	54	1.2	14	319	47	8.8	1.8	30.2	2.4	20
19/5/2011	9	376	21	130	2210	18	4.2	1.0	10.9	2.3	83
23/5/2011	9	312	33	20	4250	9.4	3.4	1.4	16.5	5.7	17
30/5/2011	14	51	*1.0*	20	692	*49*	4.2	-0.1	*70.4*	4.8	92
24/6/2011	312	8.9	1.3	2.3	34	6.7	5.5	0.9	2.6	1.5	67
7/7/2011	43	38	8.2	11	419	4.7	30	0.2	5.2	3.8	17
11/7/2011	19	156	6.7	53	650	23	4.1	0.3	10.1	1.5	75
26/7/2011	41	69	6.9	29	133	10	5.0	0.0	2.0	0.7	58
2/8/2011	26	57	*1.5*	25	103	*39*	4.5	-1.1	*7.3*	0.7	100
16/8/2011	60	50	BD	11	133	—	4.4	0.0	—	0.9	33
2/9/2011	25	125	17	18	625	7.5	7.8	1.6	4.0	2.0	100
9/9/2011	143	71	3.6	11	68	20	4.8	0.5	2.0	0.4	75
19/9/2011	5	216	48	10	872	4.5	10	0.2	1.9	1.4	33
29/9/2011	11	296	40	43	372	7.5	4.2	-0.3	1.4	0.5	67
14/10/2011	12	700	145	135	1730	4.8	11	0.5	1.3	0.9	50
21/10/2011	52	263	49	15	882	5.4	9.2	1.6	2.0	1.3	92
4/11/2011	12	849	77	125	1590	11	3.2	-0.4	2.1	0.6	58
29/11/2011	54	102	13	14	240	8.1	6.0	0.7	2.1	1.0	25
29/12/2011	1	311	79	31	728	3.9	11	0.4	0.9	0.9	25
2/1/2012	9	265	18	21	351	15	6.8	0.4	1.9	0.5	33
16/1/2012	9	126	16	12	198	8.0	3.8	0.0	1.3	0.6	42
19/1/2012	25	249	95	51	247	2.6	4.7	-0.7	0.3	0.4	75

[a] Starting date of event.

[b] The percentages of air mass travel time over the ocean were estimated using air mass back trajectories calculated using HYSPLIT (available from ARL of NOAA).

[c] DON data with relative standard deviations greater than 100% (in italic) are exclued when determining the average and median values for C/N ratio, THAA-N% and N-normalized yields of D-Ala.

[d] Below detection limit.

— Not available.

Table S2. THAA and individual amino acid concentrations (nmol L^{-1}) in precipitation samples collected at Seoul (2012–2013) and Uljin (2011–2012).

Date[a]	THAA	Asp	Glu	Ser	Thr	Gly	Arg	Ala	GABA	Tyr	Val	Ile	Phe	Leu
Seoul														
3/16/2012	229	19.7	16.8	15.1	7.9	69.8	2.7	38.1	12.1	1.7	3.4	5.1	33.4	3.7
3/23/2012	152	15.8	15.3	10.8	4.9	61.8	0.6	20.6	7.5	0.7	3.5	3.5	3.2	4.0
4/2/2012	284	36.3	33.0	10.6	12.7	102	4.5	37.1	8.2	2.6	5.8	6.3	20.5	10.0
4/10/2012	804	40.3	42.5	19.9	15.0	462	62.7	54.2	19.5	2.4	11.0	17.9	53.2	3.0
5/14/2012	296	44.0	19.8	8.5	9.5	151	4.0	31.1	8.1	0.3	2.5	2.2	13.7	1.8
6/29/2012	144	12.8	20.4	17.9	4.8	31.4	1.4	21.5	7.1	0.7	4.0	3.5	13.7	4.4
7/5/2012	34	4.1	6.9	1.1	1.2	9.8	0.2	4.5	1.9	0.1	1.2	0.8	1.4	0.6
7/10/2012	144	16.0	19.9	5.1	4.8	41.5	1.8	23.4	7.1	1.1	5.7	1.1	13.9	2.0
7/13/2012	651	52.2	49.7	23.4	17.5	311	6.2	77.3	28.6	3.8	9.7	14.5	50.4	7.2
7/14/2012	98	9.8	18.1	8.7	5.0	18.1	1.3	12.0	3.7	1.0	2.9	2.8	8.5	6.0
7/18/2012	38	4.7	7.9	4.1	1.6	6.8	0.3	4.7	1.8	0.7	1.6	1.3	1.0	1.5
7/22/2012	144	13.8	17.9	6.7	5.5	38.2	1.2	16.1	8.6	0.4	3.3	3.8	14.5	13.5
8/12/2012	129	10.8	17.4	19.4	4.6	41.9	3.0	12.8	4.0	0.4	2.9	2.5	7.1	1.8
8/14/2012	183	18.6	29.4	19.6	9.0	46.0	1.3	26.2	4.6	0.8	5.4	3.3	12.0	6.5
8/18/2012	174	15.5	29.4	33.3	8.1	33.8	0.6	20.9	2.7	1.0	5.7	3.3	15.0	5.1
8/20/2012	40	5.0	6.9	4.7	1.8	8.2	0.3	4.7	1.0	0.5	1.4	1.0	2.9	1.4
8/24/2012	94	12.1	19.4	8.2	3.9	16.6	1.6	12.8	5.2	1.0	3.5	2.5	3.9	3.0
8/30/2012	49	6.2	8.9	3.8	2.1	9.4	1.2	6.8	2.9	0.4	2.1	1.6	1.0	2.3
9/4/2012	46	4.0	5.4	2.5	1.3	15.6	0.4	5.5	2.8	0.4	1.2	1.1	2.1	4.2
9/7/2012	88	11.0	15.0	4.6	4.0	20.9	1.2	10.8	3.4	0.7	2.6	2.7	5.7	5.2
9/16/2012	23	2.8	4.3	2.6	1.1	3.4	0.8	2.6	1.3	0.3	0.8	0.5	2.1	0.5

Table S2. Continued.

10/10/2012	462	20.1	35.6	28.2	10.5	250	3.7	48.2	24.9	1.2	5.8	9.2	17.6	7.7
10/17/2012	514	39.5	60.8	55.3	16.7	195	4.8	66.2	14.1	2.8	9.1	11.4	35.3	2.7
10/22/2012	163	14.8	16.7	3.3	6.7	72.2	0.5	21.2	6.2	0.9	2.7	3.1	10.3	4.2
10/27/2012	93	8.3	9.7	8.6	3.8	35.8	0.3	8.3	2.8	0.6	2.2	2.1	8.6	1.7
11/4/2012	333	22.8	36.2	14.4	10.2	106	5.4	52.2	14.6	1.8	7.5	7.4	46.8	7.5
11/11/2012	125	11.8	31.5	15.3	5.2	24.5	2.4	13.9	3.7	1.4	3.6	2.6	6.1	3.5
11/16/2012	97	6.2	12.9	4.3	2.7	29.2	0.4	12.8	5.1	0.7	2.4	2.3	13.8	4.2
11/25/2012	196	13.3	24.5	4.8	5.7	73.5	2.0	22.3	16.3	0.6	3.2	2.8	22.2	4.3
12/5/2012	243	17.2	18.3	10.6	7.7	82.4	3.3	55.3	16.2	1.6	4.9	4.2	14.7	6.9
12/14/2012	47	4.6	8.1	4.3	1.3	12.3	0.3	6.7	2.8	0.6	1.2	1.1	2.1	1.6
12/29/2012	406	26.6	32.3	19.2	11.1	159	5.9	56.8	26.1	2.6	7.9	9.0	40.1	9.3
1/21/2013	221	16.1	19.3	4.9	5.1	63.4	0.7	18.5	7.3	1.3	3.5	4.9	30.7	45.0
2/1/2013	89	8.5	14.4	14.5	3.5	26.2	0.2	10.2	2.0	1.2	2.5	1.7	1.3	2.8
2/3/2013	89	9.3	9.0	3.0	3.8	35.2	1.1	11.2	5.2	0.3	1.3	2.0	5.0	2.9
2/5/2013	165	11.5	10.1	6.5	4.2	69.4	1.7	30.3	10.3	1.0	2.3	3.7	10.2	3.6
Uljin														
2/10/2011	356	53.4	41.4	31.2	24.1	76.8	6.0	52.0	7.0	1.2	19.4	12.9	13.8	16.7
3/5/2011	101	11.2	11.5	7.8	4.8	26.0	1.4	17.2	3.3	0.0	3.6	2.6	5.4	6.1
3/18/2011	219	28.9	25.2	14.6	9.7	67.6	5.9	30.8	6.8	0.8	8.4	5.4	7.6	7.4
3/22/2011	1140	125	202	237	62.4	253	10.6	97.6	6.3	16.1	42.7	28.3	24.4	33.9
4/7/2011	2000	307	249	110	80.3	647	121	214	41.1	10.2	67.3	43.1	65.1	46.5
4/18/2011	1980	230	224	115	109	384	304	185	33.1	16.6	100	120	71.1	81.9
4/21/2011	1170	174	219	89.0	99.9	219	29.7	124	22.7	3.1	73.8	41.4	20.9	55.6
4/25/2011	1450	199	154	74.4	70.8	502	48.8	163	16.7	5.1	57.1	38.4	83.2	38.3
4/27/2011	2170	347	421	183	119	454	62.1	250	39.8	16.4	93.0	57.5	51.2	79.5

Table S2. Continued.

5/6/2011	319	54.8	46.7	24.7	25.9	68.1	9.6	32.7	5.3	4.6	15.8	10.1	8.6	11.7
5/19/2011	2210	362	410	123	121	510	24.3	279	98.4	11.7	87.4	50.8	53.3	80.6
5/23/2011	4250	743	756	282	206	632	405	453	225	13.2	205	119	52.0	158
5/30/2011	692	78.8	92.7	56.1	32.1	235	10.9	88.6	22.0	2.9	16.0	16.8	12.3	27.8
6/24/2011	34	5.3	6.9	2.9	1.5	6.4	0.2	5.9	1.3	0.2	1.3	0.8	0.5	0.9
7/7/2011	419	51.0	78.8	78.5	18.7	120	1.7	41.5	2.6	0.7	11.0	4.5	3.7	6.3
7/11/2011	650	80.4	119	74.9	25.3	182	10.2	74.6	28.7	2.8	18.3	12.0	9.2	12.3
7/26/2011	133	18.1	17.8	8.9	6.0	43.7	2.5	18.2	3.6	0.8	3.9	2.4	3.0	4.8
8/2/2011	103	10.7	11.1	5.7	3.8	36.4	0.8	10.6	2.5	1.1	1.7	1.5	13.9	3.5
8/16/2011	133	14.3	19.9	17.5	5.1	41.4	0.6	15.8	4.5	1.0	3.5	2.8	4.2	2.4
9/2/2011	625	106	92.3	49.7	49.3	123	11.6	84.0	11.9	2.3	32.0	20.3	10.9	32.2
9/9/2011	68	9.8	8.5	7.0	3.7	18.0	0.5	10.2	1.8	0.4	2.5	1.8	2.5	1.8
9/19/2011	872	83.7	141	158	44.2	262	11.1	87.1	13.5	1.6	24.3	14.7	10.2	20.4
9/29/2011	372	37.8	44.1	20.4	11.3	86.8	64.0	46.7	10.4	1.6	7.8	9.8	27.6	3.4
10/14/2011	1728	171	211	142	137	586	33.7	177	18.5	5.6	73.7	42.6	95.3	34.4
10/21/2011	882	125	101	112	71.0	191	29.4	93.6	11.0	8.8	48.8	30.1	23.8	36.9
11/4/2011	1590	139	192	76.4	78.3	653	13.8	195	60.7	5.5	51.7	30.8	27.4	65.5
11/29/2011	240	27.3	29.0	19.4	15.5	52.9	6.9	32.5	4.8	2.3	9.9	8.7	20.5	10.5
12/29/2011	728	62.7	114	116	40.8	208	0.2	80.8	10.6	4.2	21.8	21.5	18.0	29.7
1/2/2012	351	32.2	54.8	52.5	18.9	94.3	1.2	40.6	8.0	3.1	11.8	7.8	13.9	11.8
1/16/2012	198	19.1	24.7	21.5	8.4	55.0	2.6	26.3	6.6	2.4	6.0	5.0	14.3	5.7
1/19/2012	247	26.0	27.1	17.1	14.0	88.9	1.6	27.9	5.7	0.4	6.1	2.8	20.5	9.2

[a] Starting date of event.

Table S3. D/L ratios for Asp, Glu, Ser, and Ala, and C- and N-normalized yields of D-Ala in precipitation samples collected at Seoul (2012–2013) and Uljin (2011–2012).

Date[a]	D/L ratios				Yields of D-Ala	
	Asp	Glu	Ser	Ala	nmol mg C^{-1}	nmol mg N^{-1}
Seoul						
3/16/2012	0.31	0.19	0.05	0.74	10.4	313
3/23/2012	0.35	0.27	0.06	0.77	5.8	17.5
4/2/2012	0.26	0.16	0.07	0.47	5.7	11.8
4/10/2012	0.39	0.15	0.06	0.66	11.1	167
5/14/2012	0.59	0.32	0.17	0.77	4.0	50.7
6/29/2012	0.21	0.15	0.13	0.54	10.5	83.9
7/5/2012	0.25	0.19	0.18	0.66	2.6	60.6
7/10/2012	0.54	0.33	0.03	0.78	5.8	21.7
7/13/2012	0.32	0.13	0.16	0.68	11.2	36.5
7/14/2012	0.12	0.05	ND[b]	0.27	3.3	10.6
7/18/2012	0.51	0.54	0.83	0.77	1.4	133
7/22/2012	0.21	0.13	0.06	0.41	3.7	12.6
8/12/2012	0.23	0.11	0.09	0.26	5.2	102
8/14/2012	0.20	0.15	0.22	0.35	9.1	70.3
8/18/2012	0.48	0.46	0.70	0.59	18.4	322
8/20/2012	0.50	0.41	0.59	0.63	6.4	—
8/24/2012	0.19	0.15	0.23	0.32	5.8	109
8/30/2012	0.17	0.20	0.39	0.52	2.6	138
9/4/2012	0.30	0.22	0.22	0.61	2.7	123
9/7/2012	0.16	0.08	0.03	0.40	2.9	32.0
9/16/2012	0.09	0.06	0.02	0.24	0.4	32.0
10/10/2012	0.33	0.16	0.10	0.55	—	—
10/17/2012	0.33	0.08	0.11	0.57	12.3	—
10/22/2012	0.65	0.44	0.16	0.93	6.2	145
10/27/2012	0.40	0.28	0.31	0.57	3.5	—
11/4/2012	0.27	0.22	0.06	0.81	11.9	203
11/11/2012	0.15	0.08	0.06	0.30	6.7	86.3
11/16/2012	0.45	0.45	0.08	0.77	3.5	23.9
11/25/2012	0.40	0.36	0.03	0.75	4.5	7.5
12/5/2012	0.23	0.19	0.03	0.81	18.0	265
12/14/2012	0.42	0.37	0.52	0.74	3.8	—
12/29/2012	0.38	0.33	0.05	0.79	8.7	*1470*[c]
1/21/2013	0.47	0.46	0.76	0.77	7.6	496
2/1/2013	0.52	0.56	0.54	0.70	2.2	287
2/3/2013	0.48	0.34	0.08	0.70	2.8	141

Table S3. Continued.

2/5/2013	0.37	0.48	0.15	0.89	7.5	238
Uljin						
2/10/2011	0.13	0.12	0.19	0.20	8.3	47.1
3/5/2011	0.17	0.15	0.17	0.45	12.2	438
3/18/2011	0.21	0.15	0.13	0.37	11.4	150
3/22/2011	0.08	0.05	0.02	0.17	10.2	134
4/7/2011	0.13	0.07	0.13	0.25	13.5	42.7
4/18/2011	0.13	0.09	0.03	0.16	9.2	70.6
4/21/2011	0.10	0.05	0.03	0.18	7.0	281
4/25/2011	0.19	0.09	0.16	0.18	6.4	216
4/27/2011	0.09	0.04	0.03	0.19	9.0	68.4
5/6/2011	0.15	0.09	0.12	0.16	7.0	*1920*
5/19/2011	0.13	0.06	0.04	0.29	14.0	101
5/23/2011	0.09	0.04	0.04	0.08	8.5	77.2
5/30/2011	0.22	0.10	0.05	0.45	45.6	154
6/24/2011	0.27	0.21	0.24	0.47	17.5	49.3
7/7/2011	0.12	0.09	0.08	0.27	19.2	159
7/11/2011	0.13	0.06	0.05	0.24	7.7	—
7/26/2011	0.20	0.14	0.15	0.35	5.8	41.4
8/2/2011	0.22	0.06	ND	0.43	4.7	58.4
8/16/2011	0.38	0.29	0.38	0.44	8.1	21.2
9/2/2011	0.11	0.06	0.09	0.13	6.5	27.4
9/9/2011	0.16	0.13	0.07	0.40	3.4	15.8
9/19/2011	0.14	0.05	0.03	0.19	5.5	18.6
9/29/2011	0.22	0.09	0.02	0.48	4.3	68.7
10/14/2011	0.17	0.10	0.08	0.22	3.8	52.2
10/21/2011	0.10	0.07	0.06	0.16	4.0	18.3
11/4/2011	0.38	0.40	0.10	0.62	7.3	37.2
11/29/2011	0.17	0.11	0.07	0.40	7.6	42.9
12/29/2011	0.13	0.08	0.03	0.33	5.4	7.0
1/2/2012	0.21	0.14	0.05	0.31	3.0	47.1
1/16/2012	0.27	0.19	0.11	0.57	6.3	438
1/19/2012	0.33	0.17	0.03	0.50	3.1	150

[a] Starting date of event.

[b] Not detected.

[c] Numbers in italic are outliers.

— Not available.

Publications and Presentations

Publications

Yan, G. and Kim, G.: Dissolved organic carbon in the precipitation of Seoul, Korea: Implications for global wet depositional flux of fossil-fuel derived organic carbon, *Atmospheric Environment* 59, 117–124, 2012.

Yan, G., Cho, H.-M., Lee, I. and Kim, G.: Significant emissions of ^{210}Po by coal burning into the urban atmosphere of Seoul, Korea, *Atmospheric Environment* 54, 80–85, 2012.

Yan, G., Kim, G., Kim, J., Jeong, Y. and Kim, Y. I.: Dissolved total hydrolyzable enantiomeric amino acids in precipitation: Implications on bacterial contributions to atmospheric organic matter, *Geochimica et Cosmochimica Acta*, doi:10.1016/j.gca.2015.01.005, 2015. (In press)

Yan, G. and Kim, G.: Sources and fluxes of organic nitrogen in precipitation over the southern East/Japan Sea: potential impacts on marine productivity, *Atmospheric Chemistry and Physics Discussion* 14, 31987-32025, doi:10.5194/acpd-14-31987-2014, 2014. (In review with *Atmospheric Chemistry and Physics*)

Yan, G., Kim, J., Lee, S. and Kim, G. Speciation and sources of brown carbon in the urban atmosphere of Seoul: evidence from CDOM analysis on precipitation samples. (In preparation)

Yan, G. and Kim, G. Bioavailability of dissolved organic carbon in precipitation and its relationship with chemical composition. (In preparation)

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Presentations

Yan, G. and Kim, G. (2011.12) Wet precipitation of major ions, polonium-210, and organic carbon in a metropolitan city, Seoul, Korea, American Geophysical Union Fall Meeting, San Francisco, California, USA. (Oral presentation)

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